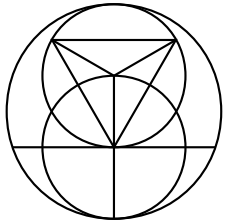

The Matter We Know

From the First Atoms to the End of the Periodic Table
Volume Two; Gatherings

Forrest Landry

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Author ORCID: 0009-0005-6275-0362

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Preface

What is the matter around us made of, and why does it hold together? This book asks what the kinds of particle make, and why what they make holds together. A *kind* of particle is a species: every electron in the universe is the same kind of thing as every other, with the same mass, the same charge and the same behavior, wherever and whenever it is found. The book's answer, given across its two volumes, has three parts. Matter is built in levels, which the book calls the *ladder of levels*: each level is made of wholes, a *whole* being anything made of parts held together, and the wholes of each level are made of the wholes of the level below. Each level is held by what the level below leaves over, and each is held far more weakly than the one below. Two rules, which come from the kinds of particle themselves, shape every level. And of every level three questions can be asked, each with its own kind of answer. Which wholes exist is a matter of *structure*: the answer follows from the kinds and their forces alone, with no measured number, as color alone permits the proton and forbids a lone quark. Which of them last is a matter of structure and measured values: the rule for lasting follows from structure, and which whole is the lightest is set by measured masses, as the measured masses make the proton last and the free neutron decay, that is, turn by itself into lighter particles. How many of each there are is a matter of *history*: it was set by what happened, as the first minutes of the universe left about a quarter of its ordinary matter as helium.

The levels are these. *Quarks*, the particles of matter that carry *color* (a name with nothing to do with visible color), the charge of the *strong force*, the force that binds quarks together, are held into protons and neutrons, which are together called *nucleons*. What holds them is the color field of the strong force, a *field* being a quantity with a value at every place in space, and the field of a force being that force's pull or push at each place. A proton or a neutron carries no color, and the colorless leftover of the col-

or field holds nucleons into nuclei; that leftover acts only between nucleons that nearly touch. A *nucleus* is the small, dense core of an atom, and an *atom* is a nucleus with electrons bound to it by the electric pull between the nucleus's positive charge and their negative ones. Atoms are held into molecules by their outer electrons: a *bond* is two atoms held together by electrons shared between them, at a lower energy than the same electrons have in the two atoms apart, and a *molecule* is atoms held together by bonds. Molecules are held to one another, into liquids and solids, by weaker pulls still.

Each level is a *rung* of the ladder, and the rungs fall in binding by many powers of ten. The *binding energy* of a whole is the energy that must be supplied to separate it into its parts. It is counted here in electron volts, an *electron volt* being the energy an electron gains in passing through a voltage of one volt, and a *voltage* between two points being the energy that each unit of charge gains or gives up in passing from one to the other. Nucleons in a nucleus are bound by up to about 8.8 million electron volts each, the electron of hydrogen by 13.598 electron volts, and molecules to one another by a hundredth to a few tenths of an electron volt (Chapter 1, Section III). On the rung above the molecule, very many wholes gathered together are held by the same bonds and weak pulls that hold the single wholes, so this rung brings no new leftover of a force; what is new on it is the number of wholes (Chapter 14, Section IV).

The two rules concern particles of spin one half, and they need four words first. *Angular momentum* is the measure of turning motion. *Spin* is the angular momentum a particle carries in itself, with no motion along a path. Both are counted in units of the *reduced Planck constant*, $\hbar$, read "h-bar": Planck's constant h, the constant of nature that relates the energy of a particle of light to its frequency, divided by 2π. A *fermion* is a particle whose spin is an odd number of halves, such as the electron, the quark and the nucleon, each of spin one half, and a *boson* is a particle whose spin is a whole number. The *state* of a particle is everything that can be found of it: where it is, how it moves, and which way its spin points.

The first rule is exclusion: no two fermions of one kind are ever found in one state. A whole made of an odd number of fermions is excluded in the same way, so that no two such wholes of one kind are found in one state, while wholes made of an even number are not excluded. Chapter 1, Section IV, shows why the count of parts decides it: swapping two such wholes swaps their fermions one pair at a time, and an odd number of those swaps acts on the wholes as a single swap of two fermions does. The second rule is that angular momentum comes in steps of $\hbar$: whole steps for motion along a path, and half steps for a particle of spin one half. So a whole made of an even number of particles of spin one half turns in whole steps, and a whole made of an odd number keeps a half.

In this volume the two rules are at work among very many wholes. Exclusion puts the electrons of a metal one to a state, from the state of lowest energy upward, so that most of them sit far above the lowest state (Chapter 6). The same rule gives a crowd of electrons or neutrons a pressure that no cooling takes away, and that pressure holds up the remnants of stars that have burned their fuel (Chapter 13). Wholes made of an even number of fermions are not excluded, so, cold enough, very many of them gather into one state, and in that state a liquid flows without friction and a metal carries an electric current, charge in motion, without loss (Chapter 9). And the whole steps of angular momentum come back in rings of such metal and in thin sheets of electrons in a magnetic field, as whole numbers that measurements on those materials count exactly (Chapter 10).

The first volume, *Wholes*, followed the wholes one at a time, or a few at a time, from the proton to the molecule. This second volume, *Gatherings*, asks what very many wholes do together. Chapter 1 restates what this volume needs from Volume One: the kinds of particle and how far each force reaches, the ladder of levels, the two rules, the size and the levels of the atom, the families of the *periodic table*, the table of the elements set out so that elements with like chemistry fall in one column, the chemical bond in its four kinds, and the nucleus with its spin. Chapter 2 finds what temperature and entropy are, *entropy* being, in everyday words, how disordered a thing is, by counting the ways in which very many particles can

share their energy, and it finds why heat flows only from hotter to colder. Chapter 3 finds why some reactions go at once and others not at all, and where a reaction settles. A reaction is held back by a barrier, a state of higher energy that the molecules must pass through on the way, and Chapter 3 finds the two routes past it, over the top and through it. Chapter 4 finds the *phases* of matter, the forms in which a substance is found, each the same throughout: gases, liquids, glasses, the soft matter between solid and liquid, and plasma, a gas whose atoms have come apart into free electrons and charged atoms. Chapter 5 finds why cool atoms repeat in *crystals*, solids whose atoms stand in one arrangement repeated through space, how their vibrations take up and carry heat, and why some solids bend while others break. Chapter 6 finds the states an electron can take in a crystal, and why metals carry an electric current, why insulators such as glass carry none, and why semiconductors such as silicon carry a little. Chapter 7 finds how the number of moving charges in a semiconductor is set on purpose, by adding atoms of other elements, and how the diode, the transistor, the light-emitting diode and the solar cell work. Chapter 8 finds why iron is a magnet and copper not, and why heat takes a magnet's alignment away at a sharp temperature. It finds also how a magnet differs from the Higgs field, the field that fills all of space and gives the particles their masses: both settled, on cooling, into one of many states that the laws of nature treat alike, but the Higgs field settled in a smooth change, with no sharp temperature. Chapter 9 finds how a liquid can flow without friction and a metal carry current without loss. It finds also that such a metal keeps a magnetic field out of itself in the same way that the Higgs field gives mass to a carrier of a force, the particle through which a force acts. Chapter 10 finds how a small piece of material can give a constant of nature to ten decimal places, from a wave that must come back to itself round a ring, from electrons bound in pairs, and from a whole number of turns that no smooth change can alter. Chapter 11 finds why light crosses glass more slowly though every wave that makes it up travels at the speed of light in empty space, and what else matter does to light. Chapter 12 finds where the nucleus shows through its atom. It

shows in *isotopes*, atoms of one element whose nuclei hold different numbers of neutrons, and in the hospital scanner. It shows in *gamma rays*, light of very high energy, given off and taken up by nuclei held so firmly in a crystal that no kick of the nucleus robs the light of energy. And it shows in the changes of nuclei that depend on the atom's electrons, and in clocks. Chapter 13 finds what holds up a *white dwarf*, the small, dense remnant left when a star like the Sun has burned out, and a *neutron star*, the collapsed core of a massive star, made mostly of neutrons. Chapter 14 looks back over the ladder of both volumes and finds what the wholes make.

A reader may begin with this volume. Every result of Volume One that a chapter here uses is restated in Chapter 1, each with the chapter of Volume One that finds it, and the two rules are given there again in full, each in its box. The later chapters cite Volume One as "Volume One, Chapter n", always with the result stated beside the citation.

The two volumes follow *The Coming of the Kinds*, which traces the universe from its first instants to the first atoms. That book ends where this one begins. At about 370,000 years, as the universe cooled through 2,973 kelvin, the electrons were bound to the first nuclei and the light went free (*The Coming of the Kinds*, Chapter 13). The *kelvin* is the unit of temperature on the scale that starts at the lowest temperature there is, with steps the size of the Celsius degree. These volumes rest on that book and on five others. The first is *The Story of the Particles*, which derives which particles exist and is the authority on that question; it is cited here as the zoo, after the physicists' name for the whole collection of particles, the particle zoo. The other four are *The Kinds of Particle*, *The Branches of the Kinds*, *The Strengths of the Kinds* and *The Measures of the Kinds*, which set out the kinds, what their structure allows and forbids, their couplings, and their masses. A *coupling* is the strength with which a particle takes part in an interaction. Those books stand without this one, so a reader who wants the full argument for a step this book takes from them finds it there.

This book takes what those books establish as its starting point and does not derive it again. Which particles exist it takes from the zoo. The couplings of the kinds it takes from *The Strengths of the Kinds*, and their masses from *The Measures of the Kinds*. That the proton is stable it takes from *The Branches of the Kinds*, Chapter 2. An *antiparticle* is a particle of the same mass as another, with its electric charge and every other such label reversed. The *neutrino*, a particle with no electric charge and a very small mass, which passes through matter almost without trace, is a Dirac particle: it is distinct from its antiparticle, the antineutrino. *The Branches of the Kinds*, Chapter 1, establishes this. From the same book this volume takes its account of the changes of nuclei that depend on an atom's electrons (this volume, Chapter 12). How the first nuclei and the first atoms formed it takes from *The Coming of the Kinds*, Chapters 12 and 13 (this volume, Chapters 1 and 2). From *The Quantum Passage* it takes two principles. The first is the *uncertainty principle*, by which the narrower the range of places in which a particle can be found, the wider the range of momenta it can be found to have, *momentum* being a body's mass times its velocity. The second is the *principle of identity*, by which what no comparison can distinguish is one thing and not two. Exclusion, the first rule, follows from the principle of identity (this volume, Chapter 1, Box 1.2). A few further results it takes from *The Coming of the Kinds* and from other books of the series, *The Kinds of Particle*, *The Basis of Physics*, *Measurement*, *The Gravitational Passage* and *The Alphabet of Particles*, each named at the place where a chapter uses it. Where a reader who comes to this book first needs something from those books, the chapter says it in plain words and then cites the place.

The book is written in two layers. The main text walks each question in words and pictures, for an interested reader who may come to this book first. Each chapter opens with a Chapter Overview, asks its question in the reader's words, and arrives at an answer said plainly. It then says, in a section called In Use, where what it found is at work in the world today, and it closes with a Summary and its Key Concepts. Each term is glossed in plain words where the reader first meets it, and is set in italics there. The

Terms at the back collect the glosses as a reminder. The derivations stand in boxes, each complete in itself, with its premises, its steps and its result, so that a physicist can check a chapter by reading its boxes in order. A first reading can pass the boxes by, since the main text states each box's result in words. Where the book draws a conclusion of its own across its chapters, it says so in the first person, where the conclusion is drawn, as Chapter 14 does when it reasons from both volumes to what is new on the rung of gatherings.

Every number that an argument of the book uses is of one of three sorts, and the text says which: derived in a box; cited as standard physics, with its source; or measured, given with its source and its uncertainty, the range within which the measurement places it. A number worked out from such values is marked as computed, so that a reader can redo the arithmetic. The measured values are gathered in one table at the back, The Measured Values Used in This Volume, and every work cited is given in full in the Bibliography. *An Immanent Metaphysics* is a work of philosophy by the author of this book, on which the books on the particles draw. Where those books tie a result to it, the Notes at the back give the tie, and the main text never needs it.

A reader needs algebra, including powers, roots and exponentials, and the idea of energy. The logarithm, which the counting of Chapter 2 uses throughout, is explained where it first enters. The main text works no calculus. In a few places it writes a rate of change, such as temperature as the change of energy over the change of entropy (Chapter 2, Section VII), and there it says in words what the symbols mean. Some boxes use a rate of change or a sum over a continuous range, and a reader who passes them by loses no result, since the main text states each one in words.

The Ladder in Brief, which follows, gives the answer in short, with a table and a figure of the ladder. When very many wholes are gathered together, what is new, and what do they make?

The Ladder in Brief

What do very many wholes do together, and why? The kinds of particle make a ladder of wholes, a whole being anything made of parts held together, and the wholes of each rung are made of the wholes of the rung below. Volume One climbed that ladder one whole at a time. Quarks are held into protons and neutrons by the color field of the strong force. That field is *confined*: it stays within wholes that carry no color, so no quark is ever found alone. Protons and neutrons are held into nuclei by the colorless leftover of that field, carried by *mesons*, each a quark with an antiquark, an antiquark being the antiparticle of a quark. The lightest meson is the pion. The mesons have mass, and a carrier with mass reaches only about its own length, the length $\hbar/(mc)$ that its mass m, $\hbar$ and the speed of light c make together. The reason is that an exchange which needs the energy of the carrier's mass can last only a short time, by the uncertainty principle, and in that time the carrier can travel only so far (Chapter 1, Box 1.1). For the pion that length is 1.41 fm, a *femtometer* (fm) being 10^{-15} m, so the leftover acts only between nucleons that nearly touch. A nucleus holds electrons into an atom by the electric pull of its positive charge. That pull reaches without bound, because the *photon*, the particle of light, which carries the electric force between charges, has no mass. Atoms hold one another into molecules by their outer electrons, shared in pairs or passed from one atom to the other, and whole molecules hold one another by weaker pulls still. Each rung is held by what the rung below leaves over, and each is held far more weakly than the one below. Chapter 1 restates these findings of Volume One, each with the chapter of Volume One that finds it.

This volume climbs the rungs above, where the wholes are very many. On the rung of gatherings, a glass of water, a copper wire and a magnet are held by the same bonds and weak pulls that Volume One found between single wholes, so this rung brings no new leftover of a force

(Chapter 14, Section IV). What is new is the number of wholes. A system of very many particles can be arranged in a vast number of complete ways with the same totals, such as the same total energy and the same number of particles, and every one of those ways counts alike. Its *entropy* is the logarithm of that count, the power to which a fixed number must be raised to give the count, a measure that adds when two systems are taken together. Its *temperature* is the energy it takes to raise its entropy by one unit, that is, to raise the logarithm of its count by one (Chapter 2). A gathering held at one temperature settles where its energy, less its temperature times its entropy, is least, so order usually wins when it is cold and disorder when it is warm (Chapter 2, Section XIV).

The orders that belong to a whole gathering are three. In a repeat, the atoms stand in one arrangement repeated through space, and the solid is a *crystal*. The set of points, one for each copy of the repeated arrangement, from which the crystal is built is its *lattice* (Chapter 5). In a held direction, the spins of a magnet's electrons line up one way, and the crystal holds that direction (Chapter 8). In a shared phase, very many wholes gather into one state, described by one wave across the whole gathering, with one *phase* throughout. The phase of a wave is the stage of its swing at a place, counted as a fraction of a whole turn of the swing; this is a second sense of the word, apart from the phases of matter, such as liquid and solid, of Chapter 4. So gathered, a liquid flows without friction, and a metal carries a steady current with no loss (Chapter 9). Each of these orders sets in at a sharp temperature, where a symmetry or a jump separates it from disorder, a *symmetry* being a change, such as a turn, that leaves a thing as it was. Where neither a symmetry nor a jump separates two arrangements, the change between them is a *crossover*, a smooth change with no jump (Chapter 2, Section XV; Chapter 4, Section V). And the motions of a gathering come in quanta, separate units of energy, that belong to the gathering alone. They are *collective excitations*, motions shared by many particles at once that come in quanta, such as the *phonon*, a quantum of vibration of a crystal's lattice; collective excitations are not kinds of particle (Chapter 5, Section IV).

The two rules of the kinds shape every rung of this volume, as they shape every rung of Volume One. By exclusion, the electrons of a crystal fill its bands from the lowest energy up, one to a state, a *band* being the set of electron states in a crystal that grow from one state of the single atom. Where the filling stops decides whether the solid is a metal, which carries an electric current, or an insulator, which carries none (Chapter 6, Section V). By exclusion too, the electrons of a star that has burned its fuel, crowded together by the star's own weight, press back with a pressure that needs no heat, and that pressure holds up a *white dwarf*, the cooling remnant of a star that has burned its fuel, about as massive as the Sun and about as large as the Earth. The electrons' pressure can hold up a white dwarf of at most about 1.4 times the Sun's mass (Chapter 13). A whole made of an even number of fermions is not excluded. An atom of helium-4 is two protons, two neutrons and two electrons, six fermions in all, and below 2.17 kelvin very many such atoms gather into one state and flow without friction. An atom of helium-3 is two protons, one neutron and two electrons, five fermions, so its atoms must first bind in pairs, each pair an even whole, which they do only below about a thousandth of a kelvin (Chapter 9, Section V). Electrons gather in the same way once they are bound in pairs, and a metal so ordered is a *superconductor*, a metal that carries an electric current with no loss, its electrons bound in pairs (Chapter 9). Photons, which are not excluded either, multiply into one state in a laser, a source of light whose beam is one state holding very many photons (Chapter 11, Section XIII). The angular momentum of motion along a path comes in whole steps because the wave of the moving particle, carried round a whole turn, must come back to itself with its phase as it was. The same rule returns in a ring of superconductor and in a thin sheet of electrons in a magnetic field, as whole numbers that measurements on those materials count exactly (Chapter 10). The *magnetic flux* through a superconducting ring, the magnetic field times the area it passes through, comes only in whole steps of h/2e, h being Planck's constant and e the electron's charge. The resistance of a sheet of electrons in a strong magnetic field stands on plateaus, flat stretches over which it does

not change as the field is changed, at $h/(\nu e^2)$, with ν, read "nu", a whole number. The value on each plateau belongs to no one material: it is the same in a layer of gallium arsenide, a crystal of gallium and arsenic, and in graphene, a sheet of carbon one atom thick, to within about one part in 10^{10} (Chapter 10).

Of every rung three questions can be asked. Which wholes and which orders exist is structure. A repeat can be turned onto itself only by a half, a third, a quarter or a sixth of a turn, and these turns, taken with mirror reflections and with the shifts of the repeat, allow 14 kinds of lattice and no more (Chapter 5, Section III). Which of these cases each substance falls in, and at what temperature its changes fall, is measured values. Silicon's *gap*, a range of energy with no electron state in the crystal, is 1.12 eV, and iron's *Curie point*, the temperature at which a magnet loses its alignment, is 1043 kelvin (Chapter 6, Table 6.1; Chapter 8, Section V). How much of each there is, and which of its allowed states a gathering keeps when it has not reached its balance, the settled state in which nothing further changes on average, is history. A *glass*, a solid whose molecules are caught in the disordered arrangement of a liquid, keeps the disorder of a liquid cooled too fast to find its rows, and a magnet keeps the direction it was last given (Chapter 14, Section VII).

Heat decides which of these orders are found in a room. Since entropy is a pure count, a temperature is an energy for each unit of entropy, and so it is measured in energy; but it is usually written in kelvin, and the *Boltzmann constant*, k, turns a temperature in kelvin into an energy (Chapter 2, Section VIII). So kT, the temperature as an energy, is 0.0259 eV at 300 kelvin, about room temperature. Set against kT, the energy that holds a structure together decides what heat does to it. A structure held by an energy far above kT is left alone by heat, one held by an energy a few times kT is broken and remade by heat all the time, and one held by an energy far below kT is found only by cooling. So nuclei and chemical bonds last at room temperature, and the weak pulls between water molecules break and remake as the water flows. An order of a whole gather-

ing is set against kT in another way: it holds below the temperature at which it sets in, and the energy given for it is kT at that temperature. So iron holds its magnetic order at room temperature, since its Curie point, 1043 kelvin, is three and a half times room temperature, and a superconductor, whose order sets in far below room temperature (at 7.19 kelvin for lead), must be cooled (Chapter 14, Box 14.1).

So the answer of this volume is this. Matter is a ladder of levels, each level of wholes held by what the level below leaves over and each held far more weakly than the one below. On the rung of gatherings what is new is number, and no new force: the counting of ways decides, at each temperature, which arrangement very many wholes take. The orders of the whole gathering, a repeat, a held direction and a shared phase, set in at a sharp temperature where a symmetry or a jump separates them from disorder. Exclusion, and angular momentum in whole steps for motion along a path and half steps for spin one half, shape every level. They shape the *shells* of atoms, a shell being a set of levels of nearly the same energy with a gap above it, and the bands of metals. They shape the gathering into one state of wholes made of an even number of fermions, and the whole numbers that rings of superconductor and sheets of electrons keep exactly. Which wholes exist is structure, which last is structure and measured values, and how many there are is history.

The Ladder as a Table

The table below sets the levels side by side, each with what holds it, its size, how strongly it is held, and the volume and chapters that argue it. Figure 1 draws how strongly each level is held, on a scale in which each step is a factor of ten.

A few words of the table are new here. An *electron volt* (eV) is the energy an electron gains in passing through a voltage of one volt; a keV is a thousand electron volts, an MeV a million, and a GeV a thousand million. A *picometer* (pm) is a millionth of a millionth of a meter, a thousand

femtometers. The table gives the size of the proton as how far its charge reaches, the radius of its charge. The radius of a nucleus grows as the cube root of A, its *mass number*, the number of its nucleons, and a nucleus is named by its element and its mass number, as helium-4, two protons and two neutrons, or iron-56. The *deuteron* is a proton and a neutron bound together. The *ground state* of an atom is its state of least energy, the state with the least of what it can lose. An *ion* is an atom or nucleus with a net charge. A free atom has no sharp edge, so the atom's row gives, at the small end, the radius of hydrogen's ground state, and at the large end the radius of the cesium ion, cesium with its outermost electron removed, as measured in crystals. How strongly an electron is held in an atom is the energy needed to remove it. The row gives that energy for the outermost electron, the most loosely held, and for the innermost electron of barium, a heavy atom whose innermost electrons are held by tens of thousands of electron volts. A *hydrogen bond* is the attraction between a hydrogen atom bound to a strongly electron-pulling atom, such as oxygen, nitrogen or fluorine, and a pair of outer electrons of another such atom (Volume One, Chapter 11, Section XIV; Chapter 1, Section VIII). The *dispersion force* is the weak pull that arises because the electrons of each atom, at any moment, sit a little off center, so that a passing separation of charge in one atom draws a matching one in the other (Volume One, Chapter 11, Section XIII; Chapter 1, Section VIII).

The ladder of levels, from the proton to the ordered states of very many wholes. Each row gives a level of matter, what holds its parts together, its size, how strongly it is held, and the volume and chapters that argue it. The small number beside each level's name leads to its note at the back, which gives the source or the computation of every value in that row; the measured values among them stand also in The Measured Values Used in This Volume.

Level	What holds it	Size	How strongly it is held	Volume and chapters

Proton and neutron[1]	the color field of the strong force, confined within the whole	the proton's charge reaches 0.84075 ± 0.00064 fm	about 99 percent of the proton's 938.272 MeV is the energy of its binding	Volume One, Chapters 2 and 3
Nucleus[2]	the colorless leftover of the color field, carried by mesons, reaching 1.41 fm	radius about $1.2\ A^{1/3}$ fm: 1.9 fm for helium-4, 7.4 fm for uranium-238	1.11 MeV for each nucleon in the deuteron; 8.79 MeV for each nucleon in iron-56 and in nickel-62, the most	Volume One, Chapters 4 to 6
Atom[3]	the electric pull of the nucleus's charge on the electrons	52.9 pm for hydrogen's ground state; 174 pm for the ion of cesium	13.598 eV for hydrogen; the outermost electron 3.894 eV (cesium) to 24.587 eV (helium); the innermost electron of barium 37.4 keV	Volume One, Chapters 7 to 10
Molecule[4]	outer electrons shared by two atoms, or passed from one to the other; between whole molecules, the hydrogen bond and the dispersion force	bonds 74.1 pm (hydrogen) to 267.3 pm (lithium)	bonds 1.0 eV (lithium) to 9.80 eV (nitrogen), 4.478 eV for hydrogen; a hydrogen bond 0.137 eV between two water molecules; the dispersion force 9.5×10^{-8} eV between two helium atoms	Volume One, Chapter 11; Volume Two, Chapter 3

Liquid and solid[5]	bonds among very many atoms or molecules at once	any size	1.113 eV for each atom of sodium metal to 8.90 eV for each atom of tungsten; 7.94 eV for each pair of ions in salt	Volume Two, Chapters 4 to 7
Ordered states[6]	in a magnet, the electric push between the electrons of neighboring atoms, sorted by their spins through exclusion, which lines the spins up; in a superconductor, the pairing of electrons	any size	0.090 eV, the Boltzmann constant times iron's Curie point, 1043 K; 0.0027 eV to break a pair of electrons in lead	Volume Two, Chapters 8 to 10

In this volume, the rows whose last column names Volume Two are argued here: how molecules change into one another in Chapter 3, liquids and solids in Chapters 4 to 7, and the ordered states in Chapters 8 to 10. Chapter 1 restates the rows of Volume One; Chapters 11 to 13 look again at the same matter, at what it does to light, at where its nuclei show through their atoms, and at what holds it up when the weight of a star presses it; and Chapter 14 sets the whole ladder side by side.

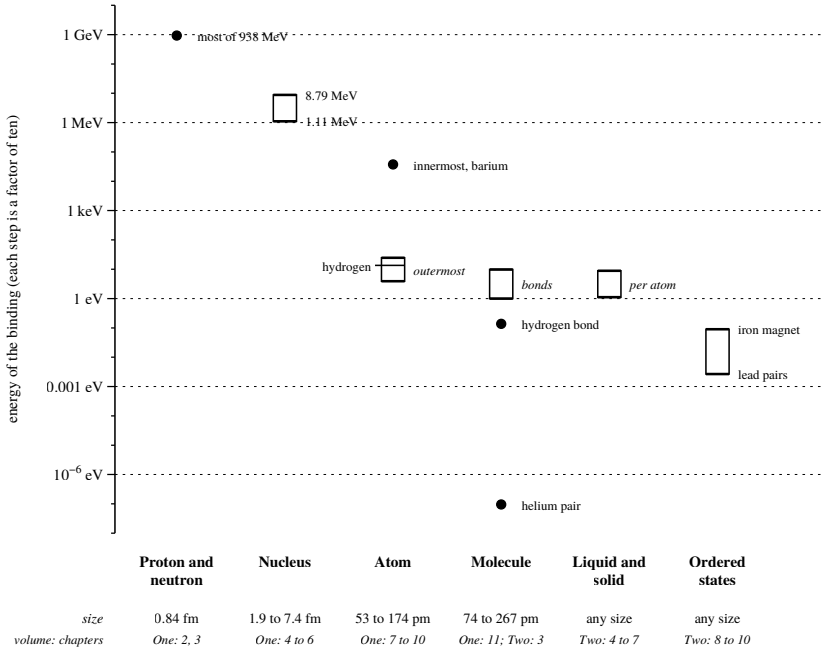


Figure 1. The ladder of levels: how strongly each level of matter is held, on a scale of energy in which each step is a factor of ten. Each column is a level, from the proton and the neutron at the left to the ordered states of very many wholes at the right. A box spans the range of the table's values for its level, and a dot marks a single value: the energy of the proton's binding, the innermost electron of barium, the hydrogen bond between two water molecules, and the dispersion force between two helium atoms. Beneath each column stand its size and the volume and chapters that argue it; the values are those of the table above.

The chapters climb this ladder from the rung of molecules upward, where the wholes become many, and each argues one stretch of it. The climb begins where Volume One left the wholes, met one at a time: what did Volume One find, and what is needed from it here?

Part One

The Counting of Many

Chapter 1

From Wholes to Gatherings

CHAPTER OVERVIEW

This chapter restates, for a reader who begins with this volume, what this volume needs from Volume One, each result with the chapter of Volume One in which it is derived. The kinds of particle are a closed list, fixed by structure, with no measured number (Section II says what structure means here). Ordinary matter is made of the few kinds that last: up and down quarks bound in protons and neutrons, and electrons, held by photons and gluons (Table 1.1). Energy and time are a *conjugate pair*, two quantities of which narrowing one widens the other, and the Incommensuration Theorem, a theorem about comparison itself, makes their bound hold at every scale. By that bound a force carried by a particle of mass m reaches about $\hbar/(mc)$ (Box 1.1). So electromagnetism reaches without bound, the weak force, which turns one kind of particle into another, about 2.5×10^{-18} m, and the colorless leftover of the color field, which is confined within wholes that carry no color, about 1.4 fm. Matter is a ladder of levels, each held by what the level below leaves over and each held far more weakly than the one below. Which wholes exist is structure, which last is structure and measured values, and how many there are is history. Two rules of the kinds shape every level. The first rule is exclusion: by the principle of identity no two fermions of one kind share a state, a fermion being a particle whose spin is an odd number of halves. A whole of an odd number of fermions is excluded in the same way, while a whole of an even number is not (Box 1.2). The second rule is that

angular momentum, the measure of turning, comes in whole steps of ħ for motion along a path and half steps for a particle of spin one half (Box 1.3). Holding an electron near a nucleus costs it energy of motion, the cost of confinement, and the balance of that cost against the electric pull gives the atom its size and its binding, for one electron held by any charge (Box 1.4). The atom's energy levels are separate, with gaps between them. Exclusion and *screening*, the partial canceling of the nucleus's charge by the inner electrons, give the periodic table its rows and its families of like elements. The bonds that hold atoms and molecules together come in four kinds: covalent, ionic and metallic, made by the atoms' outer electrons, and the weak pulls between whole molecules (Table 1.2). And the nucleus is a small, heavy core whose paired nucleons give it a spin of zero, an odd number of halves or a whole number, and, when it has spin, a *magnetic moment*, a strength as a small magnet. What is new in this volume is the number of wholes.

I. Where Volume One Leaves Us

Catch a raindrop on your finger and ask what it is made of. It is water, and water is molecules, each of two hydrogen atoms joined to one oxygen atom. Each atom is a small, heavy core with electrons bound round it. Each core is a cluster of protons and neutrons. And each proton and each neutron is made of quarks, held by a force that lets none of them go. Five times the question "what is it made of?" gets a new answer, and five times the answer is a whole made of smaller parts.

Volume One of this book began with that raindrop (Volume One, Chapter 1, Section I) and described its wholes from the bottom up, one whole at a time: one proton, one nucleus, one atom, two atoms joined. In it we asked of each whole what holds it together, how strongly, and whether it lasts. This volume describes what very many wholes do together: how a gas presses, why a crystal repeats, why copper carries an electric current and glass does not, why iron holds a magnetic direction, how a liquid can flow without friction, why light crosses glass more slowly than

empty space, and what holds up a star that has burned its fuel. Every one of those answers rests on what Volume One found about the single wholes.

A reader may begin here, with this volume, and this chapter is written for that reader. It restates, in brief, each result of Volume One that the chapters of this volume use, with the chapter of Volume One in which it is derived, so that a reader who wants the full argument knows where to find it. The two rules that shape every whole, exclusion and angular momentum in whole and half steps, are given again in full, each in its box, because nearly every chapter of this volume uses them. So the reader's question here is this: what did Volume One find, and what is needed from it here?

II. The Kinds, and How Far Each Force Reaches

Every snowflake is found a little different from every other, and two electrons are always found exactly alike, even when one was made this morning and the other in the first second of our history (Volume One, Chapter 1, Section II). A *kind* of particle is a species: every electron in the universe is the same kind of thing as every other, with the same mass, the same charge and the same behavior, wherever and whenever it is found. *The Story of the Particles*, cited in this book as the zoo, after the physicists' name for the whole collection of particles, derives every kind from the structure of comparison and shows that the list is closed. *Comparison* is the act of telling one thing from another, by which anything at all is found, and *structure*, in this book, is what follows from the form of such acts and of the kinds and forces, with no measured number. In the zoo's own words, the list "contains exactly what comparison requires and nothing else" (the zoo, Level 9, Section IV). The list is six quarks, six leptons, the photon, eight gluons, the W and Z bosons and the Higgs boson. That the list is closed matters for everything that follows: every whole in this book is built from these kinds and no others.

A *quark* is a particle of matter that carries *color*, the charge of the strong force (a name with nothing to do with visible color). The *strong force* binds quarks together. It acts only on color, and it is carried by eight *gluons*. A *lepton* is a particle of matter that carries no color. There are six kinds of lepton: the electron, its two heavier copies the muon and the tau, and three neutrinos, one partnered with each. The *neutrino* of the electron is the neutral lepton partnered with the electron. The neutrinos carry no electric charge and pass through matter almost without trace. Three forces act on these particles of matter, and each has its *carriers*, the particles through which it acts. *Electromagnetism*, the force of electric charge, of light and of every chemical bond, is carried by the *photon*, the particle of light, which carries the electric force between charges. The strong force is carried by the gluons. The *weak force* turns one kind of quark or lepton into another, as when a free neutron turns into a proton, an electron and an antineutrino, the antiparticle of a neutrino (below). It is carried by the *W boson*, which comes with positive and with negative charge, and by the neutral *Z boson*. Last comes the *Higgs boson*, the particle of the Higgs field. A *field* is a quantity with a value at every place in space, and the field of a force is that force's pull or push at each place. The Higgs field is present everywhere in space, and its value has settled: it has come to rest at a value other than zero, the same at every place, and it fills all of space with that value. That settled value gives the W and Z bosons, the quarks and the charged leptons their masses (Volume One, Chapter 1, Section II, after *The Coming of the Kinds*, Chapter 1, Section II). A particle that couples to the Higgs field meets the settled value wherever it is, and the meeting gives it an energy that it has even at rest, in proportion to how strongly it couples. An energy at rest is a mass, by Einstein's relation (below). Every particle that carries electric charge, or another label of that sort, such as the baryon number and the lepton number of this section, has an *antiparticle* distinct from itself: a particle of the same mass with its electric charge reversed, together with every other such label. The antiparticle of the electron is the *positron*, each quark has its antiquark, and each neutrino

its antineutrino. A particle that carries no such label is its own antiparticle, as the photon, the Z boson and the Higgs boson are (*The Coming of the Kinds*, Chapter 1, Section IV).

Masses of particles are given in units of energy, by Einstein's relation E = mc^2, where c is the speed of light, 299,792,458 meters per second, exact by the definition of the meter. An *electron volt* (eV) is the energy an electron gains in passing through a voltage of one volt, a voltage between two points being the energy that each unit of charge gains or gives up in passing from one to the other. The electron volt is the natural unit of energy for atoms. A million electron volts is an MeV, and a thousand MeV is a GeV.

Ordinary matter needs very few of the kinds. It is made of three kinds of particle of matter, the up quark, the down quark and the electron, held together by photons and gluons, with neutrinos passing through it. The up and down quarks are found bound in threes, in the proton (two ups and a down) and the neutron (two downs and an up), the wholes that Volume One, Chapter 2, describes. Table 1.1 gives these few, with the two wholes of three quarks beside them.

Table 1.1. The particles of which ordinary matter is made, with electric charge (in units of the proton's charge), spin (in units of ħ, which Section V explains), measured mass, and whether each lasts. The quark, electron and neutrino masses are those of Volume One, Table 1.1: the up and down quarks' from the Particle Data Group, the international collaboration that collects and reviews the measured properties of the particles, 2024, and the electron's from the Committee on Data of the International Science Council (CODATA), 2022. A quark is never found alone, so its mass is read from its effects, and the mass so read changes with the energy at which the quark is probed, since the strong force itself changes in strength with that energy. So the quark masses here are given, as physicists give them, at an energy of 2 GeV (Volume One, Chapter 1, Table 1.1). The proton's and the neutron's masses are CODATA 2022 values (Volume One, Chapter 7, Box 7.3), and the neutron's mean life is the Particle Data Group's, 2026 (Volume One, Chapter 1, Section II). Each measured value is given with its uncertainty, the range within which the measurement places it.

Particle	Charge	Spin	Mass	Lasts?
Up quark	+2/3	1/2	2.16 ± 0.07 MeV	Lasts, bound in protons and neutrons
Down quark	−1/3	1/2	4.70 ± 0.07 MeV	Lasts, bound in protons and in stable nuclei
Electron	−1	1/2	0.51099895069 ± 0.00000000016 MeV	Lasts
Neutrinos (three)	0	1/2	The heaviest about 0.05 eV (at least 0.0502 ± 0.0002 eV); the other two lighter	Last
Photon	0	1	0	Lasts
Gluons (eight)	0	1	0	Bound with the quarks; never free
Proton (two up quarks and a down)	+1	1/2	938.27208943 ± 0.00000029 MeV	Lasts
Neutron (two down quarks and an up)	0	1/2	939.56542194 ± 0.00000048 MeV	Decays when free, with a mean life of 878.3 ± 0.4 seconds; lasts inside stable nuclei

Why these last and the others do not has one answer. A particle *lasts* when it stays as it is unless something strikes it. It *decays* when, left alone, it turns into lighter particles. Every change that can happen in matter at the temperatures of the present universe keeps a few counts: electric charge; *baryon number*, the number of baryons such as protons and neutrons less the number of their antiparticles, a *baryon* being a whole of three quarks; and *lepton number*, the number of leptons such as electrons and

neutrinos less the number of theirs. The one process among the kinds that changes the baryon and lepton numbers is the sphaleron, a collective change of the field of the weak force that changes the two together by the same amount. It ran only while the universe was hotter than about 132 GeV, a temperature of some 10^{15} kelvin written as an energy, in the first instants of its history, and below that it stopped (*The Coming of the Kinds*, Chapter 4, Section II, and Chapter 5, Chapter Overview; Volume One, Chapter 1, Section II). A particle lasts when it is the lightest thing that carries the same counts as it, all of them together: then nothing lighter has its charge, its baryon number and its lepton number at once, and it has nothing lighter to turn into. Nothing lighter than the electron carries electric charge at all, so it lasts. The proton is the lightest baryon, so it lasts (*The Branches of the Kinds*, Chapter 2). The neutrinos are the lightest leptons, and the photon has no mass at all (Volume One, Chapter 1, Section II). The neutron is a baryon a little heavier than the proton, by 1.293 MeV, so a free neutron decays into a proton, an electron and an antineutrino (Volume One, Chapter 3). Its *mean life*, the average time a free neutron lasts before it decays, is 878.3 ± 0.4 seconds (Particle Data Group, 2026, as Table 1.1 gives it).

What the kinds can make is set first by how far each force reaches, and that is set by a principle about how a particle can be found, the uncertainty principle. *Momentum* is a body's mass times its velocity. The *uncertainty principle* says, of where a particle is found and how it moves, that the narrower the range of places in which it can be found, the wider the range of momenta it can be found to have. Measured by their widths, the two cannot both be made small: the width of the place, Δx, read "delta x", times the width of the momentum, Δp, is never less than $\hbar/2$. Here $\hbar$, read "h-bar", is the *reduced Planck constant*: Planck's constant h, the constant of nature that relates the energy of a particle of light to its frequency, divided by 2π, $1.054571817... \times 10^{-34}$ joule seconds, the joule being the unit of energy. *The Quantum Passage*, Chapter 4, Section III, says where the principle comes from: "The uncertainty principle is an instance of the Incommensuration Theorem". The *Incommensuration Theorem* is a theorem

about comparison itself, stated in the same book, Chapter 4, Section II: "The concepts of symmetry and continuity cannot both be simultaneously and fundamentally applied to any event or comparison. The concepts of asymmetry and discontinuity cannot both be simultaneously and fundamentally applied to any event or comparison". Its words have plain senses, which *The Quantum Passage* gives in the same chapter. Symmetry is exact sameness under a change, and continuity is smooth variation, without jumps. Asymmetry is difference, every part told apart from every other, and discontinuity is separateness, with sharp boundaries. To apply two of the four concepts (symmetry, continuity, asymmetry and discontinuity) simultaneously and fundamentally is to apply both concepts at once, and at the root of what is described. The Incommensuration Theorem is a structural fact about the nature of knowing: every finding, every result of looking or measuring, is a comparison, and the theorem holds of every comparison. A structural fact is one that follows from the form of comparison itself, and not from any particular thing compared.

The theorem gives the uncertainty principle in this way (*The Quantum Passage*, Chapter 4, Section III). A state of a particle with one exact momentum is the same all along its path: moving it along changes nothing that can be found of it, and that sameness is a symmetry. A state with one exact place marks one point of the smooth, unbroken line of places, and that is continuity. A state exact in both would join symmetry and continuity in one description of one particle, at once and at the root, and the theorem excludes that. So narrowing the place widens the momentum, and the reverse. The size of the bound, $\hbar/2$, the same book derives in its Chapter 6, Section V. And since the theorem holds of every comparison, the uncertainty principle holds at every scale of size and of energy: for an electron in an atom, for a nucleon in a nucleus, and, as the next paragraphs show, for the carrier of a force, which is why a force carried by a particle with mass has a reach. Two quantities related in this way, so that narrowing one widens the other, are called a *conjugate pair*. Place and momentum are one such pair, and *The Basis of Physics*, Essay 16, Section IV,

names others: of "every conjugate pair, energy and time, angular momentum and angle", it says that each "carries the same bound for the same structural reason".

Energy and time are the pair that sets a force's reach. Volume One, Chapter 1, Section III, described a shop that hires out tools: the dearer the tool, the sooner the shop wants it back, and so the less far it can be carried. A force acts between two particles through a carrier that passes from one to the other, and a carrier with mass is the costly tool. The energy to make it may not be there to spare, so it can be out only for a short time, and in that time it can go only so far. Box 1.1 gives the estimate.

Box 1.1. The reach of a carrier

Premises. (1) Energy and time are a conjugate pair, with the same bound as place and momentum: a state whose energy differs by ΔE from the energy the system has can be found only for a time of about $\hbar/\Delta E$ (*The Basis of Physics*, Essay 16, Section IV; *The Quantum Passage*, Chapter 4, Section III); for the size of a reach the rough form $\Delta E\, \Delta t \approx \hbar$ serves. (2) Making a carrier of mass m takes at least its rest energy, mc^2 (Einstein's relation; standard physics). (3) Nothing that carries a force moves faster than light. (4) $\hbar c = 197.3269804$ MeV fm, exact in the international units, where a *femtometer*, fm, is 10^{-15} m; the W mass is 80.3625 ± 0.0077 GeV (Particle Data Group, 2026) and the Z mass 91.1880 ± 0.0020 GeV (Particle Data Group, 2024), as Volume One, Table 1.1, gives them; the pions are the lightest *mesons*, a meson being a whole of a quark and an antiquark, and the charged pion has a mass of 139.57039 ± 0.00017 MeV (Particle Data Group, 2026).

Steps. By (1) and (2), with $\Delta E = mc^2$, the carrier can be out for a time of about $\hbar/(mc^2)$. By (3), in that time it goes at most about $c \times \hbar/(mc^2) = \hbar/(mc) = \hbar c/(mc^2)$. By (4): for the W, 197.327 MeV fm / 80,362.5 MeV = 0.00246 fm = 2.5×10^{-18} m; for the Z, 197.327/91,188.0 fm = 2.2×10^{-18} m; for the charged pion, 197.327/139.570 fm = 1.41 fm. For the photon, m = 0, and the time and the reach have no bound.

Result. A carrier of mass m reaches about $\hbar/(mc)$, the length that the carrier's mass, $\hbar$ and c make together, its *own length*: the W and the Z about 2.5 and 2.2×10^{-18} m, the pion about 1.4 fm, and the massless photon without bound. Hideki Yukawa found the exact form of a force carried by a particle with mass: its field falls with distance r as $e^{-r/\lambda}/r$, with $\lambda = \hbar/(mc)$, so beyond a few times λ it is gone (Yukawa, 1935; Volume One, Chapter 4, Box 4.1). The result is Volume One, Chapter 1, Box 1.1, restated.

The forces then sort themselves by their *reach*, the distance over which each acts. The photon has no mass, and in empty space nothing on the way absorbs or cancels its field, so electromagnetism reaches without bound, its pull falling as the inverse square of the distance (Volume One, Chapter 7, Section II). Wherever positive and negative charges come in equal amounts, as in an atom, their fields cancel at a distance, and what is left acts only on what comes close. The strong force reaches only across a proton, though its gluons have no mass either. The reason is that the gluons carry color themselves, whereas the photon carries no charge, so the gluons act on one another, and the color field between two quarks gathers into a tube whose energy grows with its length. A field whose energy grows without end as two colored particles are pulled apart never lets them go, so nothing that carries color is ever found alone. The color field is *confined*, which means that it stays within wholes that carry no color (Volume One, Chapter 1, Section III, and Chapter 2, Section VI). What acts between such wholes is a colorless leftover of the color field, carried by pairs of quark and antiquark, the lightest of which are the pions. It reaches the pion's own length, about 1.4 fm, and it is the force that holds nuclei together (Volume One, Chapter 4, Section IV). The W and Z bosons have mass, so the weak force reaches only about 2.5×10^{-18} m and acts seldom, yet it is the only force that turns a neutron into a proton or a proton into a neutron. Gravity acts on every particle, and between an electron and a proton it is weaker than the electric pull by 2.3×10^{39} (Volume One, Chapter 7, Section I). It plays no part in binding the wholes of Volume

One, and it enters this volume in two places: as the slight change of frequency of light that climbs against it (Chapter 12), and as the weight of a whole star pressing on its matter (Chapter 13).

So we now know what the kinds are and how far each force reaches. The list of kinds is closed, and ordinary matter uses only the up and down quarks and the electron, held by photons and gluons. Electromagnetism reaches without bound. The color field is confined, and only its colorless leftover acts between nucleons, out to about 1.4 fm. And the weak force reaches about 2.5×10^{-18} m.

III. The Ladder of Levels

Snap-together plastic bricks hold one another by studs on top and hollows underneath. Press one brick onto another, and some of the lower brick's studs are taken up, and the studs left free on top are what the next brick holds by. A whole wall has a row of free studs along its top, so a second wall can be built on it. The second wall holds to the first only by those few studs left over, far less firmly than each brick holds its neighbor. Volume One, Chapter 1, Section VI, used this picture for the shape of all matter, and Volume One, Chapter 12, showed it borne out on every rung.

Matter is built in levels, and each level holds by what the level below leaves over. Quarks are held by the color field into protons and neutrons, which are together called *nucleons*. The binding is so strong that most of a proton's mass is the energy of it. Of its 938 MeV, the three quarks supply about 9 MeV, and the color field, the motion and binding of the quarks and the gluons, supplies the rest (*The Strengths of the Kinds*, Chapter 6, Section I, as Volume One, Chapter 2, Section VII, gives it). A nucleon carries no color: its color field is held wholly within it. What it leaves over is the colorless leftover of Section II, which holds nucleons into a *nucleus*, the atom's small, dense core. A nucleus carries no color either, but it carries the positive charge of its protons, and that charge holds electrons round it into an *atom*, a nucleus with electrons bound to it by the electric pull

between the nucleus's positive charge and their negative ones. An atom carries no net charge, but its outermost electrons can be shared or passed between atoms, and those hold atoms into molecules, a *molecule* being atoms held together by bonds. And the passing separations of charge of whole atoms, each a moment in which an atom's electrons sit a little off center, with the nearly bare protons of some molecules, hold molecules to one another into liquids and solids (Volume One, Chapter 12, Section III).

Each level is held far more weakly than the one below. The *binding energy* of a whole is the energy that must be supplied to separate it into its parts. Nucleons in a nucleus are bound by up to about 8.8 MeV each, the most near iron and nickel (Volume One, Chapter 4, Section VII), against the more than 900 MeV that the color field puts into each nucleon. Hydrogen holds its electron by 13.598 eV (Volume One, Chapter 7, Section IX), some half a million times less than a nucleus holds each of its nucleons. A hydrogen molecule holds its two atoms together by 4.48 eV, and every chemical bond lies between about 1 and 10 eV (Volume One, Chapter 11, Section XV). And molecules hold one another by about 0.01 to 0.3 eV (Volume One, Chapter 11, Box 11.2): the heat of a kettle boils water into separate molecules without breaking any molecule apart.

The largest fall, from the nucleus to the atom, is about a million in energy, to within a factor of a few, and it has a plain reason (Volume One, Chapter 12, Box 12.1). Confining a particle costs energy, by the uncertainty principle: a particle held within a distance r has a momentum of at least about $\hbar/r$, and the energy of its motion is its momentum squared over twice its mass (standard physics). So the cost of confinement, for a particle of mass m confined within a distance r, is about $\hbar^2/(2mr^2)$, and it grows as one over the square of the region and as one over the mass (Box 1.4). A nucleon is held within about 1.84 fm of its neighbors, a distance set by the short reach of the force between nucleons. An outer electron is held within about the size of an atom, some thirty thousand times wider, a size set by the small strength of electromagnetism. That width counts twice, squared, while the nucleon's mass, 1836 times the electron's, counts only once, so the cost for a nucleon in a nucleus, about 6.1 MeV, stands about

half a million times above the cost for an electron in an atom, about 13.6 eV (computed). The measured bindings, 8.8 MeV for each nucleon against 1 to 10 eV for each chemical bond, stand at about one million to nine million times, so the computed and the measured ratios are both a million to within a factor of a few.

Three questions can be asked of every rung, and each has its own kind of answer (Volume One, Chapter 1, Section VI, and Chapter 12, Section VI). Which wholes exist is structure: the kinds and the forces permit some wholes and exclude others. Which of them last is structure and measured values. A whole lasts when it is the lightest thing that carries its counts, and that rule is structure. Which whole is the lightest is set by measured masses, as Volume One, Chapter 3, shows for the proton and the neutron. How many of each there are is history. Helium-4 carries a quarter of the mass of ordinary matter because of what the first minutes of the universe did (*The Coming of the Kinds*, Chapter 12). Carbon, oxygen and iron are as plentiful as they are because of what the stars did since (Volume One, Chapter 6). In the zoo's words, "The zoo tells us which particles exist. It does not tell us how many of each the universe contains" (Level 4, Section IV).

So we now know the shape of what Volume One found. Matter is a ladder of levels, quarks into nucleons, nucleons into nuclei, nuclei and electrons into atoms, atoms into molecules, molecules into larger gatherings, each level held by what the level below leaves over and each held far more weakly than the one below. Two rules of the kinds shape every level, and the next two sections give them.

IV. Two of a Kind Cannot Share a State

Save a letter on a computer as a file named "letter" in a folder. Then save a second copy, the same in every character, under the same name in the same folder. Afterward the folder holds one file, not two. Nothing about the second copy would tell it from the first, so there is nothing for the folder to keep apart.

Particles of one kind are like those copies, and the reason is a principle about comparison (Volume One, Chapter 1, Section IV). *Angular momentum* is the measure of turning motion: for a body going round a center, its momentum times its distance from the center, and in general the quantity that is kept because the laws of nature are the same in every direction. Kept here means that the total stays the same, for bodies left to themselves, through every change they undergo. That a sameness of the laws keeps a quantity in this way is a theorem of Emmy Noether's (Noether, 1918): since no direction of space is singled out, nothing can alter the total turning of bodies left to themselves. A particle can carry angular momentum in itself, with no motion along a path, and that is its *spin*, counted in units of ħ. A *fermion* is a particle whose spin is an odd number of halves, such as the electron, whose spin is one half. A *boson* is a particle whose spin is a whole number, such as the photon. The quarks and leptons, the particles of matter, are fermions, and the carriers of the forces are bosons. The *state* of a particle is everything that can be found of it: where it is, how it moves, and which way its spin points.

The *principle of identity* is stated in *The Quantum Passage*, Chapter 8, Section VI: "The principle of identity says that what no comparison can distinguish, in any way at all, even in principle, is one thing and not two". Two electrons are alike in every way that any measurement can register (Section II). If two electrons were in one state, no comparison could tell which was which. So, in the words of the same section, two particles of matter of one kind in one state "could not be told apart, so they would be

one instance": two electrons in one state would be one electron. So no two fermions of one kind are ever found in one state. The rule that no two fermions of one kind are ever found in one state is the *exclusion principle*. Wolfgang Pauli found the exclusion principle in 1925 as the rule that orders the electrons of atoms (Pauli, 1925). Physicists usually reach it through a theorem that Pauli proved in 1940 with the help of the theory of relativity, Einstein's account of space, time and motion (Pauli, 1940). In *The Quantum Passage* it follows from the principle of identity alone, and "the theorem of Pauli is not used" (Chapter 8, Section VI), so the rule rests on nothing beyond the sameness of particles of one kind.

The carriers of the forces stand the other way, and the same principle says why. A particle of matter is a separate thing, counted one by one: two electrons are two, and nothing in one electron is more or less of an electron than in another. A carrier is an amount of a field, as a wave of light is: two waves of one shape in one place add to one wave of twice the strength. So, by the principle of identity, two electrons in one state would be one electron, and the states of two electrons hold no state with both in one. But two photons in one state are one state of light with twice the amount, and the states of many photons hold every such state. A photon added to a photon in one state is that state with twice the light, so any number of photons can share a state, as the light of a laser shows. The particles of matter all have spin one half, and the carriers have whole spin. So exclusion, which the principle of identity gives to the particles of matter, falls on exactly the particles of spin one half, the fermions, and never on the bosons (Volume One, Chapter 1, Section IV).

Box 1.2 sets out the argument in full, and in words it runs as follows. Swap the two particles of a pair, then swap them back, and the pair is as it was. So one swap can do only one of two things to a state of the pair: leave it unchanged, or turn it into its exact opposite, every part of it reversed in sign. Every state of two particles of one kind is a sum of a part that the swap leaves unchanged and a part that it reverses, and the states with both particles in one state build up exactly the unchanged part. The principle of identity removes those states for two particles of matter, so what is

left is the reversed part: swapping two electrons always reverses the sign of their state. A state with both electrons in one state would then have to equal its own reverse, as a number would have to equal its own negative, and only zero does, so there is no such state.

Box 1.2. Exclusion from the principle of identity

Premises. (1) The principle of identity: "what no comparison can distinguish, in any way at all, even in principle, is one thing and not two" (*The Quantum Passage*, Chapter 8, Section VI). (2) Two particles of matter of one kind in one state, written ψ (read "psi"), could not be told apart by any comparison, so they would be one particle: the states of two such particles hold no part in which both are in one state, written $\psi \otimes \psi$ ("ψ with ψ") (premise 1; the same section). (3) Exchanging two particles of one kind twice restores the state, so the exchange has two values: a state it multiplies by $+1$ is symmetric, and a state it multiplies by -1 is antisymmetric; every state of two such particles is a sum of a symmetric part and an antisymmetric part; and the states $\psi \otimes \psi$, taken over every ψ, build up exactly the symmetric states (mathematics, the linear algebra of pairs; the same section). Premise (2) holds for every ψ alike, so the set of states that two such particles can take is unchanged when the states of both particles are changed in the same way; and the only sets of states of a pair with that property are the symmetric states, the antisymmetric states, and the two together (mathematics, the same linear algebra). (4) The particles of matter, the quarks and leptons, have spin one half; the carriers of the forces have spin one, and the Higgs boson spin zero (the same section). (5) For a carrier, a second one in a state already filled adds to the amount in that state, so the states of many carriers hold every $\psi \otimes \psi$ (the same section).

Steps. By (2) and (3), the states of two particles of matter of one kind are one of the three sets of (3); the symmetric states hold every $\psi \otimes \psi$, so the set is the antisymmetric states: exchanging the two particles multiplies the state by -1. An antisymmetric state with both particles in ψ is $\psi \otimes \psi - \psi \otimes \psi$, which is zero: there is no such state. By (4), the particles of matter are the fermions, so no two fermions of one kind share a state. By (5) and (3), the states of many carriers are the symmetric states, which hold any

number in one state. Now take two wholes of one kind, each made of n fermions, each in the same inner state, and exchange them as wholes. That exchange swaps each fermion of the first with its partner in the second, n swaps in all, each multiplying the state by -1, so the state is multiplied by $(-1)^n$.

Result. No two fermions of one kind share a state; any number of bosons of one kind can. A whole made of an odd number of fermions changes sign when exchanged with another of its kind, so it is excluded as a fermion is; a whole made of an even number does not change sign, so it is not excluded. This holds whenever two wholes are exchanged as wholes, each in the same inner state, which is the case at energies too small to reach inside them. The rule for exchanging fermions, bosons and wholes is Volume One, Chapter 1, Box 1.2, restated.

The same swap settles the rule for wholes. Take two wholes of one kind, such as two protons, each in the same inner state, and swap them as wholes. That swaps each part of the first with its partner in the second: for two protons, three swaps of quarks. Each swap of two fermions reverses the sign of the state, so an odd number of swaps reverses it, and an even number leaves it as it was. A whole made of an odd number of fermions therefore reverses the sign of the state when it is swapped with another of its kind, as one fermion does, and it is excluded as a fermion is. A whole made of an even number does not reverse the sign, and it is not excluded. This holds whenever the wholes are swapped as wholes, at energies too small to reach inside them.

The rule for wholes sorts every whole of the ladder. A whole can be counted at any depth, and the answer is the same at each, since a nucleon is three quarks, an odd number, and so counts as an odd number of fermions however it is counted. A proton is three quarks, an odd number of fermions, so two protons exclude one another, and so do two neutrons, and each kind of nucleon fills its own levels in a nucleus (Volume One, Chapter 4, Section III). A hydrogen atom is a proton and an electron: two fermions counted as a nucleon and an electron, or four counted as three

quarks and an electron, an even number either way. So a hydrogen atom is not excluded by another hydrogen atom, though the electron inside it excludes every other electron of the same state. An atom of helium-4, two protons, two neutrons and two electrons, is six fermions, an even number, and is not excluded. An atom of helium-3, with one neutron fewer, is five, an odd number, and is excluded (Volume One, Chapter 12, Section V). Counted down to quarks and electrons the two atoms are fourteen and eleven, an even and an odd number again. Chapter 9 of this volume describes what that one difference does to the two heliums when they are cooled.

Exclusion is also why matter is solid to the touch. Volume One, Chapter 1, In Use, described a hand pressed on a table: both are almost wholly empty space. What stops the hand is that the electrons of its atoms cannot take the states the table's electrons already hold. So pushing the two together would confine the electrons more tightly, into states of higher energy. Confinement costs energy, by the uncertainty principle: a narrower region means a wider range of momenta, and so more energy of motion (Section III). Freeman Dyson and Andrew Lenard proved that matter made of nuclei and electrons is stable in bulk, because the electrons are fermions (Dyson and Lenard, 1967). Stable in bulk means that its least energy grows only in proportion to the number of its particles, so that twice the matter holds twice the energy and no more, and a heap of matter does not fall in on itself as it grows.

The same difference between fermions and bosons is why ordinary physics finds light as waves and matter as particles. Carriers are not excluded, so many carriers can share one state. When very many of them share one state with one definite phase, the strength of their field is definite, since the spread of that strength is small beside the strength itself (mathematics, the limit of large numbers), and together they are a wave of definite field: for photons, the classical field, the field of light as the physics before quantum mechanics describes it. Particles of matter are excluded, so no two of one kind share a state, and for them there is no such limit of many in one state. In the limit in which the phase of a particle's

wave, the stage of the wave's swing (The Ladder in Brief), runs through very many whole turns along each way it could take, particles of matter are found one by one, each along its own way: the way on which that phase is stationary, so that a small change of the way leaves the phase unchanged, apart from an amount far smaller than the change (Chapter 11, Section V, states the same rule for the rays of light). So ordinary physics finds light as waves and matter as particles because the carriers are not excluded and the particles of matter are.

Which state of very many photons is that wave? When the number of photons in one state of light is definite, their phase is not, and so the field they give averages to zero over many findings: a definite number of photons does not give a definite field. The wave of definite field is the limit in which the number of photons grows large while their state is a combination of states of different numbers with one definite phase, so that the strength of the field is definite and the spread of that strength is small beside the strength itself (standard quantum mechanics of light). That combination is called a *coherent state*, and the condition that the field be definite fixes it.

So we now know the first rule. Two fermions of one kind are never found in one state, because two that could not be told apart would be one. Bosons of one kind crowd into one state freely. And a whole of an odd number of fermions is excluded, while a whole of an even number is not.

V. Turning Comes in Steps

Watch the minute hand of a clock. In one hour it makes one whole turn, and it stands exactly where it began. Now hold the buckle of a belt whose other end is fixed to a table, and turn the buckle once about the belt's length. The belt is left with a twist that no moving of the buckle, without turning it, can undo. Turn the buckle a second time in the same sense, and

the double twist can be undone: carry the buckle round the belt in a loop, keeping its direction fixed, and the belt hangs flat again. The hand returns after one turn; the belt returns only after two.

Particles turn in both of these ways (Volume One, Chapter 1, Section V, and Chapter 7, Section VI). A particle going round a center, as an electron goes round a nucleus, has *orbital angular momentum*, the angular momentum of that motion. A particle also has its spin, angular momentum in itself with no motion along a path (Section IV). The second rule of the kinds says how much of each a particle can have: angular momentum is counted in steps of ħ, whole steps for motion along a path, and half steps for a particle of spin one half.

Orbital angular momentum is the clock hand. A turning is found only against something that does not turn with it, and the electron's turning about the nucleus is found against the nucleus. The angle of the electron about the nucleus is a relation between two things found, the electron and the nucleus, so one whole turn brings that angle back to itself, as the minute hand comes back to the twelve. A particle is found as a wave, the length of its wave fixing its momentum (Volume One, Chapter 7, Section IV), and a wave that runs round a center must fit the turn. The angle and the angular momentum are a conjugate pair (Section II), and an angular momentum conjugate to an angle that closes on itself after one whole turn can take only whole multiples of ħ: zero, one, two and so on, in either sense. Spin is the belt. *The Kinds of Particle*, Chapter 1, Section VIII, shows that a particle which carries its own placement round with it returns to its starting state only after two full turns. To carry its placement round with it is for its relation to everything around it to turn with it, as the belt's twist turns with the buckle. The same section shows that the least spin such a particle can have is one half, in units of ħ, and it gives the other case in one line: "Whole-step spin (0, 1, ...) is possible for what returns after one turn." A particle of spin one half is found with its spin along any axis as one of two values, $+1/2$ or $-1/2$, in units of ħ. Box 1.3 carries the argument.

Box 1.3. Whole steps from the closing angle, and half steps for spin

Premises. (1) The angle φ (read "phi") of a particle about a center, measured about a chosen axis, and the orbital angular momentum about that axis, L_z, are a conjugate pair: L_z generates turns of the angle as momentum generates shifts of place, so that L_z acts on the particle's wave $\psi(\varphi)$ as $-i\hbar\, d/d\varphi$, with i the square root of -1 (*The Basis of Physics*, Essay 16, Section IV; *The Quantum Passage*, Chapter 4, Section III, and Chapter 6, Section V, for the pair of place and momentum). (2) The angle is a relation between two things found, the particle and the center, so one whole turn returns it to itself: $\psi(\varphi + 2\pi) = \psi(\varphi)$. (3) A particle that carries its own placement returns only after two whole turns, $\psi(\varphi + 4\pi) = \psi(\varphi)$, while one turn reverses its sign (*The Kinds of Particle*, Chapter 1, Section VIII). (4) "Two half-integer spins can add to zero or to one, but they cannot add to one-half, and any orbital motion of the two adds only whole units" (*The Story of the Particles*, Level 3, Section III).

Steps. A state of definite $L_z = \lambda$ (read "lambda") satisfies $-i\hbar\, d\psi/d\varphi = \lambda\psi$, so $\psi(\varphi) = e^{i\lambda\varphi/\hbar}$. By (2), $e^{i\lambda 2\pi/\hbar} = 1$, so $\lambda/\hbar$ is a whole number m: $L_z = m\hbar$, with $m = 0, \pm 1, \pm 2$, and so on. The same holds about every axis; the total orbital angular momentum, whose square is $l(l + 1)\hbar^2$, takes $l = 0$, 1, 2 and so on, and along any one axis it is found as $m\hbar$, with m running in whole steps from $-l$ to $+l$, which is $2l + 1$ values. By (3), a return only after 4π allows $e^{i\lambda 2\pi/\hbar} = -1$ as well, so $\lambda/\hbar$ may be a half: the half steps of spin. By (4), applied one pair at a time, a whole made of an even number of particles of spin one half has a whole-number spin, and a whole made of an odd number keeps a half, whatever the orbital motion of its parts.

Result. Orbital angular momentum comes in whole steps of $\hbar$, zero included; spin comes in half steps for a particle of spin one half; a whole of an even number of such particles turns in whole steps, and a whole of an odd number keeps a half. The result is Volume One, Chapter 7, Box 7.2, restated, with the rule for wholes of Volume One, Chapter 1, Section V.

The whole steps and the half steps are one result about what stays the same. An *invariant* is whatever stays the same under every change of setting, a setting being anything about how and from where a thing is found that can be changed without changing the thing, such as the direction from which it is viewed. *The Basis of Physics*, Essay 1, Section V, draws the consequence from the Incommensuration Theorem. An invariant is symmetric, the same under every change of setting. Followed to the limit of finding, that is, found as finely as anything can be found, it cannot also vary continuously, since the Incommensuration Theorem forbids symmetry and continuity together at the root. *The Basis of Physics* states the consequence: "It is discontinuous. It is discrete. The invariant comes as a countable thing: so many quanta of charge, so many units of angular momentum, one electron or two but not one and a half", quanta being separate units. Angular momentum is the invariant that belongs to turning, and so it comes as a countable thing: in whole steps for a motion that closes on itself after one turn, in half steps for a particle of spin one half. Finding the angle more finely, by any process however fast, only widens the range of angular momenta found, since the two are a conjugate pair. It never finds a value between the whole steps (Volume One, Chapter 7, Section VI).

Here the two rules, exclusion and the steps of angular momentum, apply together. A whole of an odd number of fermions keeps a half step of spin, so it is a fermion by its spin, and it is excluded by Box 1.2. A whole of an even number has whole-number spin, so it is a boson by its spin, and it is not excluded. The proton, three quarks, has spin one half, the deuteron, a proton and a neutron, has spin one, and the helium-4 nucleus has spin zero (Volume One, Chapter 4, Section III). Every whole in this book is sorted by these two rules together.

So we now know the second rule. Angular momentum is counted in steps of $\hbar$: whole steps, zero included, for motion along a path, and half steps for a particle of spin one half. Wholes of an even number of such particles turn in whole steps, and wholes of an odd number keep a half. So no particle or whole is ever found with a spin of a quarter, or with an orbital angular momentum of half a step.

VI. The Atom's Size and Its Levels

Press a guitar string against a fret halfway along its length and pluck it, and the note jumps an octave: only half the string is free, so its longest wave is half as long, and a shorter wave is a higher note. Volume One, Chapter 7, Section IV, used that string for an electron: confine a wave to less room and it must be made of shorter waves, and for an electron a shorter wave means a larger momentum. Confinement has a cost, paid in motion, and the uncertainty principle of Section II sets it: an electron confined within a distance r carries a momentum of at least about $\hbar/r$.

The *hydrogen atom* is a single proton with a single electron bound to it. The electric pull between them falls as the inverse square of their distance, *Coulomb's law*, because the field of a charge goes out alike in every direction of three-dimensional space and nothing on the way absorbs or cancels it (Volume One, Chapter 7, Section II). The pull is a force, and $\hbar c$ divided by the square of a distance is also a force, since $\hbar c$ is an energy times a length. So the pull between two charges of the proton's size, at a distance r, is a pure number times $\hbar c/r^2$, the same number at every distance. That number is α, read "alpha", the *fine-structure constant*, the strength of electromagnetism, 1/137.035999177 (CODATA 2022; Volume One, Chapter 7, Section III), so the pull is $F = \alpha\hbar c/r^2$. Bringing the electron closer gains energy from the pull and costs energy of confinement, and the cost rises faster than the gain as the electron comes in. The *ground state* of a system is its state of least energy, the state with the least of what it can lose (Volume One, Chapter 7, Section V). Having nothing further to give up, it sends nothing out, which is why the electron in an atom does not spiral into the nucleus. Hydrogen's ground state lies where the cost and the gain balance, and Box 1.4 derives it for one electron held by any charge, with a mass left free so that later chapters can use it.

Box 1.4. One electron held by a charge

Premises. (1) A particle of mass m confined within a distance r has a momentum of about $\hbar/r$, by the uncertainty principle (Section II); taking the momentum as $\hbar/r$ gives an energy of motion $\hbar^2/(2mr^2)$ (Volume One, Chapter 7, Section IV and Box 7.1). (2) Its electric energy at a distance r from a fixed charge Ze, Z times the proton's charge, is $-Z\alpha\hbar c/r$, by Coulomb's law with the pull $Z\alpha\hbar c/r^2$ (Volume One, Chapter 7, Section III, and Chapter 9, Section II). (3) $\hbar/(m_e c) = 386.15927$ fm, from $\hbar c = 197.3269804$ MeV fm and $m_e c^2 = 0.51099895069$ MeV; $\alpha = 1/137.035999177$ (CODATA 2022).

Steps. The total energy is $E(r) = \hbar^2/(2mr^2) - Z\alpha\hbar c/r$. Its slope, $dE/dr = -\hbar^2/(mr^3) + Z\alpha\hbar c/r^2$, is zero at $r = \hbar/(mcZ\alpha)$. There $E = Z^2\alpha^2 mc^2/2 - Z^2\alpha^2 mc^2 = -Z^2\alpha^2 mc^2/2$. The momentum there is $\hbar/r = mcZ\alpha$, so the speed is $Z\alpha c$. For the electron's mass and $Z = 1$, by (3): $r = 386.15927$ fm $\times$ $137.035999 = 52{,}917.72$ fm $= 0.529 \times 10^{-10}$ m, and $\alpha^2 m_e c^2/2 = 0.51099895$ MeV$/(2 \times 137.035999^2) = 13.6057$ eV, the binding with the proton held fixed (the Rydberg energy), with the speed $\alpha c = 2{,}188$ km/s.

Result. One particle of mass m held by a fixed charge Ze has its ground state at the distance $\hbar/(mcZ\alpha)$, with a binding of $Z^2\alpha^2 mc^2/2$, moving at $Z\alpha c$. For the electron held by a fixed charge of the proton's size these are the *Bohr radius*, $a_0 = \hbar/(m_e c\alpha) = 0.529 \times 10^{-10}$ m, and a binding of 13.6057 eV, the *Rydberg energy*. A heavier particle is held closer and more tightly, both in proportion to its mass, and a charge Ze holds its particle Z times closer and Z^2 times more tightly than the proton does. The balance fixes how the size and the binding depend on the mass, the charge and α, and the full solution of Schrödinger's equation, the equation that gives the waves of an electron held by a charge, fixes the number in front of each. That solution gives exactly the radius and the energy found here (Volume One, Chapter 7, Box 7.1, after *The Strengths of the Kinds*, Chapter 1, Section IV), so taking the momentum as $\hbar/r$ in (1), with no further factor, gives

the exact ground state. The size and the energy found here are Volume One, Chapter 7, Box 7.1, and Chapter 9, Section II, restated with the mass and the charge left free.

The proton is not quite fixed. Volume One, Chapter 7, Section IX, described a grown man and a small child face to face on ice skates pushing apart: both move, and the heavier one moves less. The proton is 1836 times heavier than the electron, so it moves 1836 times less, and the exact account replaces the electron's mass by the *reduced mass*, $m_e m_p/(m_e + m_p)$, the electron's mass made smaller by about one part in 1836. With it hydrogen's binding is 13.598 eV, and 13.6 eV is its rounded form. One electron bound to a nucleus of any charge is a *hydrogen-like ion*, and Box 1.4 gives it directly: ionized helium, $Z = 2$, holds its electron by about 54.4 eV, four times the Rydberg energy (Volume One, Chapter 9, Section II). And wherever an electron is held by a pull made weaker, or carries a mass made different, by its surroundings, the same balance gives its size and its binding, as Chapter 7 of this volume shows for an electron held in a crystal.

Above the ground state lie the atom's other states, and they come in separate energy levels, each a set of states of one energy, with gaps between. An energy level, a set of states of one energy, is a second sense of the word level, apart from the levels of the ladder of matter. The wave of a bound electron must close on itself, as a skipping rope swings in one, two or three loops and never in one and a half (Volume One, Chapter 7, Section VII). So it has a whole number of *radial nodes*, spheres about the nucleus on which the wave is zero, and its orbital angular momentum takes whole values l (Box 1.3). The energy level's number, the *principal quantum number*, is $n = n_r + l + 1$, with n_r the number of radial nodes, and hydrogen's energy levels lie at $-13.6\ \text{eV}/n^2$. States with $l = 0$, 1, 2 and 3 are called s, p, d and f states, and a state of the electron in an atom is called an *orbital*, each orbital having its own shape. Energy level n holds the states with $l = 0$ up to $n - 1$, each with its $2l + 1$ orientations, so it holds $1 + 3 +$

$5 + ... = n^2$ states of motion. States of different l share one energy in hydrogen because the inverse-square pull keeps one more quantity than other pulls toward a center keep: the quantity that, for a planet on its orbit, is the direction of the orbit's long axis. With the electron's two directions of spin, energy level n holds $2n^2$ states (Volume One, Chapter 9, Box 9.1). An atom gives out light, or takes it in, only when its electron passes from one level to another, so the light comes only at the wavelengths that match the differences of the levels: a *spectrum*, the light sorted by wavelength, of sharp lines (Volume One, Chapter 7, Section VII).

The electron is also a small magnet. How strong a small magnet a body is, measured by the turning push that a magnetic field of a given strength gives it, is its *magnetic moment* (Volume One, Chapter 8, Section II). The natural unit of an electron's moment is the *Bohr magneton*, $e\hbar/(2m_e)$, the moment of one unit $\hbar$ of orbital angular momentum, with e the proton's charge. The electron's spin, though only half a unit, carries one whole Bohr magneton, because its moment follows the whole turn of its placement (Section V). Its *g-factor*, the ratio of a particle's magnetic moment to the value its angular momentum alone would give, is 2 (Volume One, Chapter 8, Box 8.1). Inside the atom the electron's spin magnet meets a magnetic field: seen from the electron itself, moving with it, the nucleus's electric field sweeps past, and an electric field that moves is found as a magnetic field as well. That meeting, *spin-orbit coupling*, splits each energy level into a few close ones, the *fine structure*, smaller than the spacing of the levels by about α^2 in hydrogen and growing steeply with the nuclear charge (Volume One, Chapter 8, Section III, and Chapter 10, Section VI). In the heaviest atoms it grows to nearly an electron volt, and Section VII returns to it there.

And hydrogen lasts. Hydrogen has charge zero, baryon number one and lepton number one, and the only other state with those counts that could lie below it is a neutron with a neutrino. That state is heavier than a hydrogen atom by 0.782 MeV, the 1.293 MeV by which the neutron outweighs the proton less the 0.511 MeV of the electron, so hydrogen has

nothing lighter to change into (Volume One, Chapter 7, Box 7.3). Chapter 13 of this volume describes what happens when the electrons of a star are pressed hard enough to bring that 0.782 MeV themselves.

So we now know the atom's size and its levels. An electron confined near a nucleus pays in motion for its confinement, and the balance with the pull sets the ground state: hydrogen's at the Bohr radius, 0.529×10^{-10} m, bound by 13.6 eV, and an electron of any mass held by any charge in proportion (Box 1.4). The energy levels are separate, at -13.6 eV$/n^2$ for hydrogen, with $2n^2$ states in level n, and atoms take in and give out light only at the lines between them.

VII. The Periodic Table's Families

Dmitri Mendeleev laid out cards for the elements in order of weight and found the properties coming round again, row after row, so that he could leave gaps for elements not yet found (Mendeleev, 1869; Volume One, Chapter 9, Section I). Volume One, Chapter 9, showed why the table has that shape, and Chapter 10 showed where it ends.

Atoms are counted by the charge of their nucleus, the number Z of its protons, the *atomic number*. An atom of atomic number Z holds Z electrons, and they take the states of Section VI, set by their radial nodes, their orbital angular momentum l and their spin. No two electrons of an atom share a state (Box 1.2), so in the ground state the electrons fill the states from the lowest energy up, each taking a state of its own. A *shell* is a set of energy levels of nearly the same energy with a gap above it. In an atom the shell n is the set of states with one value of n, which share one energy when only the nucleus holds the electron, and it holds $2n^2$ electrons: 2, 8, 18 and 32. A *subshell* is the part of a shell with one value of l, such as 2p or 3d, and it holds $2(2l + 1)$ electrons, two for s, six for p, ten for d and fourteen for f.

The electrons already placed change the order in which the rest fill. Charges which gather round a charge cancel its field at a distance, and this canceling is called *screening* (Volume One, Chapter 7, Section II). In an atom the inner electrons screen part of the nucleus's charge from the outer ones, which find an *effective nuclear charge*, the true charge Z less the part the electrons between hide. A state of lower l reaches closer to the nucleus, inside the screening electrons, so it is screened less and lies lower. So within a shell s lies below p, p below d and d below f, and the d and f subshells are lifted above the s subshell of the next shell (Volume One, Chapter 9, Section VI). *Madelung's rule* states the result: with screening, the subshells fill roughly in order of n + l, and, at a tie, lower n first (Volume One, Chapter 9, Box 9.2). That order gives the rows of the table, its *periods*, of 2, 8, 8, 18, 18, 32 and 32 elements. The first period ends with the filled 1s subshell and every later one with a filled p subshell, at helium, neon, argon, krypton, xenon, radon and oganesson.

The columns of the table are its *groups*, and the elements of one group make up one of the table's families, which behave alike because each period repeats the outer arrangement of the one before (Volume One, Chapter 9, Section VIII). A subshell with every one of its states taken, a *closed subshell*, has no preferred direction, and at the end of each period the next state open to an electron lies across a gap, in a new shell. So the *noble gases* of the last column, helium to oganesson, neither take nor give electrons easily, and they hardly combine with anything. The *ionization energy* of an atom, the energy that must be supplied to free its most loosely held electron, shows the gap. It falls from helium's 24.6 eV to lithium's 5.4 eV, and from neon's 21.6 eV to sodium's 5.1 eV (Volume One, Chapter 9, Table 9.2, from Kramida et al., 2024). The atom just after a noble gas has one electron outside a closed core that screens nearly all of the nucleus's charge from it, so it gives that electron up easily. The atoms just after the noble gases are the *alkali metals* of the first column, lithium to francium. Beside the alkali metals stand the *alkaline earth metals*, beryllium to radium, with two outer electrons. The atom one electron short of closing its p subshell takes an electron readily. The energy set free when a neutral atom takes

one more electron, its *electron affinity*, is largest for these, the *halogens*, fluorine to tennessine: 3.61 eV for chlorine (Volume One, Chapter 9, Section VIII, from Andersen, Haugen and Hotop, 1999). The electrons beyond an atom's last closed subshell are its *valence electrons*, and they are the ones that take part when atoms join.

In the middle of the table an inner subshell fills beneath outer electrons already placed, so the atoms change little from one to the next. The atoms in the middle of the table are the *transition metals* of the d block, the ten columns in which a d subshell fills. Most alike of all are the *lanthanides* and the *actinides* of the f block, the two rows of fourteen in which an f subshell fills. The lanthanides and the actinides are named for lanthanum and actinium, which begin the two rows of the f block (Volume One, Chapter 9, Section IX). And within a partly filled subshell the electrons fill with their spins aligned first, one to each orientation. Two electrons with aligned spins are alike in their spins, so the reversal of sign that a swap brings (Section IV) falls on their waves of place, and the joint wave of the two vanishes where they would meet: they keep apart. So they screen each other less and are held more strongly by the nucleus (*Hund's first rule*; Volume One, Chapter 9, Section X). An atom with a partly filled subshell therefore carries a net spin, and with it a magnetic moment: iron, cobalt, nickel and gadolinium most of all. In Chapter 8 of this volume we carry those aligned spins from one atom to a whole piece of iron.

In the heaviest atoms the innermost electron moves at about $Z\alpha$ times the speed of light, more than half of it from gold on (Box 1.4; Volume One, Chapter 10, Section II). As that speed nears the speed of light, the energy of the electron's motion counts as added mass, and Box 1.4 showed that a heavier particle is held closer, so the s states, which reach the nucleus, draw in. The d and f states, screened more by the drawn-in s states, swell, and spin-orbit coupling grows to split subshells by nearly an electron volt (Volume One, Chapter 10, Sections V to VII). So gold is yellow, taking up the blue light that silver passes, and mercury is liquid (Volume One, Chapter 10, Sections VIII and IX). The table ends where nuclei end. A table of atoms with point nuclei would end near $Z = 137$, and of atoms

with nuclei of their true size near Z = 170 to 173, but nuclei split first, and the heaviest element made is oganesson, Z = 118 (Volume One, Chapter 10, Sections III and IV).

So we now know the families. Exclusion places the electrons one to a state, from the lowest energy up, and screening orders the subshells, by n + l with the lower n first. That order makes periods of 2, 8, 8, 18, 18, 32 and 32. Their closed subshells make the noble gases, their lone outer electrons the alkali metals, their atoms one electron short the halogens, and their partly filled inner subshells the transition metals, the lanthanides and the actinides, and the magnetic atoms among them.

VIII. The Chemical Bond in Its Four Kinds

Two loudspeakers playing one note fill a room with loud places and quiet places: where the two waves arrive with the same sign they reinforce, and where they arrive with opposite signs they cancel (Volume One, Chapter 11, Section II). This adding of waves is called *interference*, and Volume One, Chapter 11, finds the whole of the chemical bond in it, since an electron's state is a wave.

An electron held by two nuclei at once has a state built from its states about each nucleus. Taken with the same sign, the two parts add between the nuclei, more of the electron lies where both nuclei pull on it, and its energy is lower than about either nucleus alone. Taken with opposite signs, the parts cancel between the nuclei, and the energy is higher. So one level of each atom becomes two levels of the pair, a lower one, the *bonding state*, and a higher one, the *antibonding state*, the higher raised more than the lower is lowered (Volume One, Chapter 11, Box 11.1). The bonding state holds the two nuclei together at the separation of least energy, the *bond length*, and two atoms so held by electrons in a lower shared state make a *bond*. By exclusion the bonding state takes two electrons of opposite spin and no more, so each bond is completed by a pair of electrons of opposite spin in the lower shared state. The hydrogen molecule, two pro-

tons and a pair of electrons, is 74 pm long, a picometer being a millionth of a millionth of a meter, and is bound by 4.48 eV (Volume One, Chapter 11, Section IV, from Liu et al., 2009). Two atoms with closed subshells would fill the antibonding state as well as the bonding one, and since it is raised more, they push apart: helium stays single, and closed shells keep their distance (Volume One, Chapter 11, Section V).

Only the outer electrons join, so each atom forms as many bonds of an electron pair as the smaller of two numbers: its outer electrons, and the electrons it lacks to complete its subshell. That number is its *valence*, and it recurs with the periods: carbon four, nitrogen three, oxygen two, fluorine one, and silicon, phosphorus, sulfur and chlorine the same below them (Volume One, Chapter 11, Section VI). A pair of an atom's outer electrons that takes no part in its bonds is a *lone pair*. The p states point along the three directions of space. Combined with the s state, as waves are combined in interference, they point as far apart as their number allows, so bonds point and molecules have shapes. The four bonds of carbon point to the corners of a solid with four triangular faces, 109.47 degrees apart (Volume One, Chapter 11, Section VII).

Bonds come in four kinds, by how the outer electrons are shared, and Table 1.2 sets them side by side. A *covalent bond* is a bond made by a pair of electrons shared between two atoms, and it points. Where one atom draws the shared pair more strongly, the pair sits nearer it, and the bond is a *polar bond*, a covalent bond whose shared pair sits nearer one atom than the other. At the extreme the electron passes over entirely. In an *ionic bond* one atom gives up an electron to another, and the two, now ions of opposite charge, an *ion* being an atom or nucleus with a net charge, are held by the electric pull alone. That pull has no direction, so each ion gathers round it as many of the opposite charge as fit: six, in salt (Volume One, Chapter 11, Section X). In the *metallic bond* each atom gives its few loosely held outer electrons to be shared with all its neighbors at once, so the shared electrons move through the whole piece of metal and the bond between the atoms has no direction (Volume One, Chapter 11, Section XII). And whole molecules, whose outer electrons are already paired in

their bonds, hold one another by two weak pulls. The *dispersion force* is the weak pull that arises because the electrons of each atom or molecule, at any moment, sit a little off center, and each such passing separation of charge in one induces a matching one in the other, so that the two attract. It acts between all atoms and molecules (Volume One, Chapter 11, Section XIII). The *hydrogen bond* is the attraction between a hydrogen atom bound to a strongly electron-pulling atom, such as oxygen, nitrogen or fluorine, and a lone pair of another such atom. It is stronger than the dispersion force and weaker than a covalent bond (Volume One, Chapter 11, Section XIV, and Box 11.2).

Table 1.2. The four kinds of bond, with an example of each and the energy needed to pull the example apart, as Volume One, Chapter 11, Table 11.2, gives them. Energies: H_2, Liu et al. (2009); N_2, Greenwood and Earnshaw (1997); HCl, Huber and Herzberg (1979); salt, Kittel (2005), from the crystal to free ions; sodium and tungsten, Kittel (2005), from the metal to free atoms, for each atom; the water pair, Rocher-Casterline et al. (2011); the helium pair, Grisenti et al. (2000).

Kind	**In plain words**	**Example**	**Energy to pull apart (eV)**
Covalent bond, and its unequal form, the polar bond	a pair of electrons shared between two atoms in a lower shared state; in a polar bond the pair sits nearer one atom	H_2; N_2 (three pairs); HCl	4.48; 9.8; 4.4
Ionic bond	an electron passed over entirely, the two ions held by the electric pull alone, without direction	salt, NaCl	7.94 for each pair of ions
Metallic bond	loosely held outer electrons shared with all the neighbors at once, without direction	sodium; tungsten	1.1; 8.9 for each atom

Weak pulls between whole molecules: the hydrogen bond and the dispersion force	a nearly bare hydrogen drawing a lone pair of another atom, with a direction; passing separations of charge in two atoms, lined up so that they attract	two water molecules; two helium atoms	0.137; about 0.0000001

Every covalent, ionic and metallic bond rearranges the states of the atoms' outer electrons, which are about the atom's own size, and the energies of such states are of the size of the Rydberg energy of Box 1.4, $\alpha^2 m_e c^2/2$, about 13.6 eV. So every such bond's energy is a fraction of the Rydberg energy, set by the measured values of its atoms: the charges, the sizes and the screening of the particular atoms, and bonds lie between about 1 and 10 eV. The dispersion force and the hydrogen bond, which share no pair, lie below, at about 0.01 to 0.3 eV (Volume One, Chapter 11, Section XV). The nuclei, thousands of times heavier than the electrons, nearly stay at rest in a bond, so the electrons' states depend on the nuclei's charges and places and hardly at all on their masses. So *isotopes*, different forms of one element with the same number of protons and different numbers of neutrons, bond almost alike (Volume One, Chapter 11, Section XVI). A bond holds its nuclei like a spring, and its vibration comes in quanta, separate equal amounts of energy, with a least energy of half a quantum that no cold takes away, the *zero-point energy* (Volume One, Chapter 11, Section XVI; Chapter 3 of this volume).

So we now know the chemical bond. An electron's state about two nuclei is a wave whose parts add or cancel, and the lower state, filled by a pair of electrons of opposite spin, is the bond. By how the outer electrons are shared, bonds are covalent, polar on the way to ionic, ionic, metallic, or the weak pulls between whole molecules. A covalent, ionic or metallic bond holds with about 1 to 10 eV, and whole molecules hold one another with about 0.01 to 0.3 eV. The covalent, ionic and metallic bonds and the pulls between whole molecules are the bonds that hold the four kinds of solid of Chapter 5 of this volume.

IX. The Nucleus and Its Spin

At the center of every atom of Sections VI to VIII sits its nucleus, and chemistry has treated it as a point of charge. It is small: a hydrogen atom is some sixty thousand times wider than its proton, from the Bohr radius, 0.529×10^{-10} m, against the proton's 0.84 fm (Volume One, Chapter 1, In Use). And it is heavy: a proton has 1836 times the electron's mass, and every other nucleus more (Volume One, Chapter 7, Section IX). Volume One, Part Two, found what a nucleus is.

A nucleus is counted by three numbers: its *mass number* A, the number of its nucleons; its *proton number* Z, the number of its protons, which is its charge and the atomic number of its element; and its *neutron number* N, the number of its neutrons, with $A = Z + N$ (Volume One, Chapter 4, Section I). Nuclei of one element with different numbers of neutrons are its isotopes (Section VIII). The nucleons are held together, against the electric push of the protons, by the colorless leftover of the color field, carried by mesons and reaching about the pion's own length, 1.41 fm (Box 1.1; Volume One, Chapter 4, Section IV). Pressed closer than about half a femtometer, nucleons push apart, the *repulsive core* (Volume One, Chapter 4, Section V), so they sit about a nucleon's width apart and each keeps its identity. With so short a reach each nucleon holds only its neighbors, so every nucleus has the same density inside, about 0.16 nucleons in each cubic femtometer, and its radius is about $1.2\ A^{1/3}$ fm (Volume One, Chapter 4, Section VI). The binding for each nucleon rises from the lightest nuclei, peaks at about 8.8 MeV near iron and nickel, and falls beyond (Volume One, Chapter 4, Section VII). So *fusion*, the joining of light nuclei into a heavier one, and *fission*, the splitting of a heavy nucleus into lighter ones, both set energy free.

Inside the nucleus the two rules, exclusion and the whole and half steps of angular momentum, work as they do in the atom. A nucleon is three quarks and so a fermion, so no two protons and no two neutrons

share a state. Each kind of nucleon fills its own energy levels from the lowest up, two to a level, one for each direction of spin (Volume One, Chapter 4, Section III). Two protons, or two neutrons, in one level with opposite spins add to spin zero and bind more strongly than either alone, because a pull of short reach gains most when the two share one region: that gain is the pairing of nucleons (Volume One, Chapter 4, Section VII). A pull of short reach binds two particles only when its strength passes a threshold. Two nucleons in their lowest state can have their spins aligned, adding to spin one, or opposite, adding to spin zero. Two nucleons of one kind sit in the same state of motion, so by exclusion their spins must be opposite, and only a proton with a neutron can take the arrangement with aligned spins. That arrangement holds more strongly, and it alone passes the threshold: the *deuteron*, the nucleus of a proton and a neutron, of spin one, is the only bound pair of nucleons (Volume One, Chapter 4, Box 4.3). Two protons and two neutrons fill the lowest level of each kind with both spins, and the helium-4 nucleus, the *alpha particle*, is bound by 28.30 MeV, far more than its neighbors (Volume One, Chapter 4, Section VIII). The energy levels of a nucleus fall into shells, sets of levels of nearly the same energy with a gap above, which close at 2, 8, 20, 28, 50, 82 and 126 nucleons of one kind, the *magic numbers*. They close there because in a nucleus the coupling of each nucleon's spin with its orbital motion is strong, and the level whose spin is aligned with its orbital motion lies lower. In the higher sets of levels that coupling carries the aligned level down across the gap into the shell below (Volume One, Chapter 4, Section IX).

The spin of a nucleus is the sum of its nucleons' spins and their orbital angular momenta, the whole taken as one, and the two rules and the pairing set it (Volume One, Chapter 4, Section IX). In a nucleus with an even number of protons and an even number of neutrons every nucleon is paired with one of its kind, and its ground state has spin zero. In a nucleus of odd mass number one nucleon is left unpaired, and the whole keeps a half (Box 1.3), so its spin is one half or more. The proton's is one half, and oxygen-17, whose odd neutron sits above a closed shell in a level of total angular momentum five halves, its orbital motion and its spin taken

together, has spin 5/2. In a nucleus with an odd number of protons and an odd number of neutrons the two unpaired nucleons add to a whole number, as the deuteron's spin of one shows. A nucleus with spin is a magnet. For the same angular momentum a moment goes as the charge over the mass. So the natural unit of a nucleus's moment is the *nuclear magneton*, the moment of one unit ħ of orbital angular momentum carried by a charge e with the proton's mass, 1/1836 of the Bohr magneton (Volume One, Chapter 3, Section VII). The proton's moment is 2.793 nuclear magnetons and the neutron's −1.913, the neutron's showing that it has charged parts (Volume One, Chapter 3, Section VII). The moment of a nucleus with one unpaired nucleon lies near the moment that nucleon would carry alone in its level (Volume One, Chapter 4, Section IX, after Schmidt, 1937). Chapter 12 of this volume finds where these small magnets show through the atom round them.

Which nuclei last was Volume One, Chapter 5's question. A nucleus lasts when no set of products it could change into, with every kept count kept, has less mass, and 251 nuclei have never been seen to decay (Volume One, Chapter 5, Section I). The others change, in three ways (Volume One, Chapter 5, Sections II, VII and X). In *beta decay* a neutron of the nucleus turns into a proton, or a proton into a neutron, by the weak force, with an electron, or a positron, the electron's antiparticle, given off with a neutrino. In alpha decay a heavy nucleus sends out an alpha particle, which passes through the barrier of the electric push that it has too little energy to climb, because its wave reaches past the region that confines it. And a nucleus left in a state above its lowest falls by giving off a *gamma ray*, light of very high energy. A free neutron decays, setting free 0.782 MeV, the 1.293 MeV by which it outweighs the proton less the 0.511 MeV of the electron it gives off. But a neutron inside a stable nucleus lasts, because turning it into a proton would cost more than that, the new proton having to take a level above every proton already there (Volume One, Chapter 5, Section V). The first minutes of the universe made hydrogen and helium-4 with traces of a few light nuclei, and the stars made the rest: carbon, oxygen and iron in their burning, and the nuclei beyond iron by taking in

neutrons (Volume One, Chapter 6, Sections IV to VI). They took them in slowly in red giants, stars swollen large and cool late in their lives, and rapidly where two neutron stars merge. A *neutron star* is a body about as massive as the Sun, or more, packed to the density of a nucleus and made mostly of neutrons, the collapsed core of a massive star.

So we now know the nucleus. It is a small, heavy core of protons and neutrons held by the colorless leftover of the color field, all at one density, and its nucleons pair and fill shells. Its spin is zero when every nucleon is paired, an odd number of halves when the mass number is odd, and a whole number when both counts are odd. And with spin it is a magnet of a few nuclear magnetons, far weaker than the electron.

X. From One Whole to Very Many

Every whole of Volume One was met one at a time, or a few at a time, each in its ground state or near it (Volume One, Chapter 12, Summary). The things of the world are gatherings. A glass of water, a copper wire, a magnet, a star: each is a gathering of more wholes than anyone could count one by one, all moving, all exchanging energy with one another. Volume One, Chapter 11, Table 11.2, closes its list of the kinds of bond with two words that are not bonds at all, heat and temperature: properties of very many particles sharing energy among themselves, which need a counting of the ways those particles can share it. That counting is where this volume begins.

The two rules of Sections IV and V apply to every gathering. Fermions of one kind, crowded together, must take states of their own, so they fill their states from the lowest energy up to a top. How full their states are determines whether a solid carries an electric current, and what holds up a star that has burned its fuel. Wholes of an even number of fermions are not excluded, so, cooled and crowded, they can gather into one state, and photons, which are not excluded either, can be multiplied into one state as the light of a laser. And the whole steps of angular momentum, which

Volume One counted for one electron about one nucleus, come back as whole numbers counted exactly in rings of cold metal and in thin sheets of electrons in a strong magnetic field.

This volume takes these up in four parts. Part One, The Counting of Many, of which this chapter is the first, counts the ways very many particles share their energy (Chapter 2), follows how molecules change and where their changes settle (Chapter 3), and finds the phases of matter, gases, liquids and the soft things between solid and liquid (Chapter 4). Part Two, Solids, finds why cool atoms repeat (Chapter 5), how the electrons of a crystal take their states in bands (Chapter 6), and what is built by setting on purpose how many charges can move in a semiconductor (Chapter 7). Part Three, Order Among Many, finds how a magnet holds a direction (Chapter 8), how wholes made of an even number of fermions gather into one state and flow without loss (Chapter 9), and how matter keeps whole numbers exactly (Chapter 10). Part Four, Matter Seen Again, finds what matter does to light (Chapter 11), where the nucleus shows through its atom (Chapter 12), and what holds up matter pressed by the weight of a star (Chapter 13). In Chapter 14 we then look back over the whole ladder.

So we now know what this volume needs from Volume One: the kinds and their reach, the ladder, the two rules, the atom, the table's families, the four kinds of bond and the nucleus with its spin, each restated above with the chapter of Volume One that finds it. What is new here is the number of wholes.

In Use

The families of the periodic table are used every day by people who choose an element for what its outer electrons will do.

An airship is lifted by a gas lighter than air, and the two lightest gases sit side by side at the top of the table and behave in opposite ways. Hydrogen has one electron and lacks one to close its 1s subshell, so it bonds

readily, and with the oxygen of the air it burns, its atoms rearranging their bonds into water and giving out the difference of the bonds' energies. The airship Hindenburg was filled with hydrogen, and on 6 May 1937, while docking at Lakehurst, New Jersey, it caught fire and was destroyed, and 36 people died (standard accounts of the Hindenburg disaster). Helium has its 1s subshell closed, so it neither takes nor gives an electron easily, its ionization energy, 24.6 eV, the largest of any atom (Volume One, Chapter 9, Table 9.2), and two helium atoms push apart where two hydrogen atoms bond (Section VIII). Blimps rely on the pressure of their lifting gas, "usually helium, rather than flammable hydrogen" (standard accounts of blimps): the closed shell is what makes the lifting gas safe.

Welders use the next noble gas down. When a metal is melted to join two pieces, the hot metal would combine with the oxygen of the air. In gas tungsten arc welding, the weld and its electrode are "protected from oxidation or other atmospheric contamination by an inert shielding gas", argon or helium (standard accounts of gas tungsten arc welding), oxidation being the joining of a metal with oxygen. Argon, which closes the third period with a filled 3p subshell, takes part in no reaction with the hot metal, though it is pressed against it.

And the battery of a telephone uses the first member of the alkali metals. Lithium's outer electron sits alone in a new shell outside a closed core that screens nearly all of the nucleus's charge from it, so lithium gives up that electron readily. Measured against hydrogen, the voltage at which lithium gives up its electron in a cell, −3.0401 volts, is the most negative of the table, and a lithium-ion cell gives 3.6 or 3.7 volts (Chapter 3 of this volume, In Use, with its sources). A noble gas guarding a weld, a closed shell lifting an airship safely, and an alkali metal's lone electron driving a current are the families of Section VII at work.

Summary

Volume One followed the wholes of matter one at a time, and I restate what this volume needs from Volume One. The kinds of particle are a closed list fixed by structure, and ordinary matter is made of the few that last, the up and down quarks bound in protons and neutrons, and electrons, held by photons and gluons. A particle lasts when it is the lightest thing that carries the same counts of charge, baryon number and lepton number, all of them together (Table 1.1). By the conjugate pair of energy and time, whose bound the Incommensuration Theorem makes hold at every scale, a carrier of mass m reaches about $\hbar/(mc)$ (Box 1.1). So the photon reaches without bound, the weak force's W and Z about 2.5×10^{-18} m, and the colorless leftover of the confined color field, carried by mesons, about 1.4 fm.

Matter is a ladder of levels, each held by what the level below leaves over and each held far more weakly than the one below. Nucleons are held by the color field, nuclei by its colorless leftover at MeV, atoms by the nucleus's charge at electron volts, molecules by outer electrons at 1 to 10 eV, and molecules to one another by weak pulls at hundredths and tenths of an electron volt. Which wholes exist is structure, which last is structure and measured values, and how many there are is history.

Two rules of the kinds shape every level. By the principle of identity, two fermions of one kind in one state could not be told apart and so would be one, so no two share a state, while bosons crowd into one state freely. A whole of an odd number of fermions is excluded, and a whole of an even number is not (Box 1.2). Angular momentum comes in whole steps of $\hbar$, zero included, for motion along a path, because the angle about a center closes after one turn, and in half steps for a particle of spin one half, which returns only after two. Wholes of an even number of such particles turn in whole steps, and wholes of an odd number keep a half (Box 1.3).

An electron near a nucleus pays in motion for its confinement, and the balance with the pull places hydrogen's ground state at the Bohr radius, bound by 13.6 eV, and an electron of any mass held by any charge in proportion (Box 1.4). The energy levels are separate, $2n^2$ states in level n, and light comes and goes only at the lines between them. Exclusion and screening fill the atoms' subshells in order of n + l and make periods of 2, 8, 8, 18, 18, 32 and 32, with the noble gases, the alkali metals, the halogens, the transition metals, the lanthanides and actinides, and the magnetic atoms as their families. An electron held by two nuclei has a lower state, which a pair of electrons of opposite spin fills to make the bond, and bonds are covalent and polar, ionic, metallic, or the weak pulls between whole molecules (Table 1.2). The nucleus is a small, heavy core of nucleons at one density, which pair and fill shells. So its spin is zero when every nucleon is paired, an odd number of halves when its mass number is odd, and a whole number when both counts are odd, and with spin it is a magnet of a few nuclear magnetons.

What is new in this volume is the number of wholes. A glass of water holds about 10^{25} molecules; how can anything be said about so many?

✶

KEY CONCEPTS

- **Kind of particle.** A species: every particle of one kind is the same as every other, with the same mass, charge and behavior, wherever and whenever it is found; the list of kinds is closed.
- **Quark; color; strong force; gluon.** A quark is a particle of matter that carries color, the charge of the strong force; the strong force binds quarks, acts only on color, and is carried by eight gluons.
- **Lepton; neutrino.** A lepton is a particle of matter that carries no color; the neutrino of the electron is the neutral lepton partnered with the electron.

- **Electromagnetism; photon.** The force of electric charge, of light and of every chemical bond; the photon, the particle of light, carries the electric force between charges.
- **Weak force; W and Z bosons.** The force that turns one kind of quark or lepton into another, carried by the W bosons, positive and negative, and the neutral Z boson.
- **Field.** A quantity with a value at every place in space; the field of a force is that force's pull or push at each place.
- **Carrier of a force.** The particle through which a force acts between two others.
- **Higgs boson.** The particle of the Higgs field, a field present everywhere in space whose settled value gives the W and Z, the quarks and the charged leptons their masses.
- **Antiparticle; positron.** A particle of the same mass as another, with its electric charge and every other such label reversed; the positron is the electron's antiparticle.
- **Electron volt (eV); MeV; GeV.** The energy an electron gains in passing through a voltage of one volt; a million and a thousand million electron volts.
- **Particle Data Group; CODATA.** The international collaboration that collects and reviews the measured properties of the particles; the Committee on Data of the International Science Council, whose recommended values of the constants this book uses.
- **Baryon; meson; baryon number; lepton number.** A whole of three quarks; a whole of a quark and an antiquark; the number of baryons less the number of their antiparticles; the number of leptons less the number of theirs; every change at the temperatures of the present universe keeps both numbers and the electric charge.
- **Lasting and decaying.** A particle lasts when it stays as it is unless something strikes it, and it does so when it is the lightest thing that carries the same counts of charge, baryon number and lepton number, all of them together; otherwise, left alone, it decays into lighter particles.

- **Momentum; angular momentum.** A body's mass times its velocity; and the measure of turning motion, for a body going round a center its momentum times its distance from the center, kept because the laws of nature are the same in every direction.
- **Spin; orbital angular momentum.** The angular momentum a particle carries in itself, with no motion along a path; and the angular momentum of a particle's motion about a center.
- **Reduced Planck constant ($\hbar$).** Planck's constant h divided by 2π, $1.054571817... \times 10^{-34}$ joule seconds; the unit in which angular momentum is counted.
- **Uncertainty principle.** The narrower the range of places in which a particle can be found, the wider the range of momenta it can be found to have: $\Delta x\, \Delta p \geq \hbar/2$; an instance of the Incommensuration Theorem, true at every scale of size and of energy.
- **Incommensuration Theorem.** Symmetry and continuity cannot both be simultaneously and fundamentally applied to any event or comparison, nor asymmetry and discontinuity; a structural fact about the nature of knowing.
- **Conjugate pair.** Two quantities of which narrowing one widens the other: place and momentum, energy and time, angle and angular momentum.
- **Femtometer (fm).** 10^{-15} m, about the size of a proton.
- **Reach of a force; own length.** The distance over which a force acts; for a carrier of mass m, about its own length $\hbar/(mc)$, the length that its mass, $\hbar$ and c make together; for the massless photon, without bound.
- **Confinement; the cost of confinement.** The keeping of the color field within wholes that carry no color, so that no colored particle is found alone; and, in a second sense of the word, the confining of any particle to a small region, which costs it an energy of motion of about $\hbar^2/(2mr^2)$ for a particle of mass m within a distance r (Box 1.4).

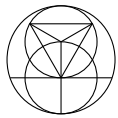
- **Atom; nucleus; nucleon; molecule.** An atom is a nucleus with electrons bound to it by the electric pull between the nucleus's positive charge and their negative ones; the nucleus is its small, dense core of protons and neutrons, together called nucleons; a molecule is atoms held together by bonds.
- **Binding energy.** The energy that must be supplied to separate a bound whole into its parts.
- **The ladder of levels.** Matter built in levels, quarks into nucleons, nucleons into nuclei, nuclei and electrons into atoms, atoms into molecules, molecules into larger gatherings, each held by what the level below leaves over and each far more weakly than the one below.
- **Fermion and boson.** A particle whose spin is an odd number of halves, such as the electron; and a particle whose spin is a whole number, such as the photon.
- **State.** Everything that can be found of a particle: where it is, how it moves, and which way its spin points.
- **Principle of identity.** What no comparison can distinguish, in any way at all, even in principle, is one thing and not two (*The Quantum Passage*, Chapter 8, Section VI).
- **Exclusion principle.** No two fermions of one kind share a state; it follows from the principle of identity; a whole of an odd number of fermions is excluded, a whole of an even number is not (Box 1.2).
- **Invariant.** Whatever stays the same under every change of setting; found as finely as anything can be found, it comes as a countable thing.
- **Whole and half steps.** Orbital angular momentum in whole steps of ħ, zero included, because the angle about a center closes after one turn; spin in half steps for a particle of spin one half, which returns only after two (Box 1.3).
- **Hydrogen atom; hydrogen-like ion.** A single proton with a single electron bound to it; one electron bound to a nucleus of any charge.

- **Coulomb's law; fine-structure constant (α).** The electric force between two charges falls as the inverse square of their distance; α, the strength of electromagnetism, a pure number, 1/137.035999177, with the pull between unit charges $F = \alpha\hbar c/r^2$.
- **Ground state.** A system's state of least energy, the state with the least of what it can lose.
- **Rydberg energy.** $\alpha^2 m_e c^2/2 = 13.606$ eV, the binding of one electron held by a fixed charge of the proton's size; hydrogen's own binding, with the proton's small motion, is 13.598 eV.
- **Bohr radius.** The size of hydrogen's ground state, $a_0 = \hbar/(m_e c\alpha) = 0.529 \times 10^{-10}$ m, where the cost of confinement balances the pull (Box 1.4).
- **Reduced mass.** $m_e m_p/(m_e + m_p)$ in hydrogen, the electron's mass made smaller by about one part in 1836, because the proton moves a little too.
- **Radial node; principal quantum number; s, p, d and f states; orbital.** A sphere about the nucleus on which the electron's wave is zero; $n = n_r + l + 1$; states with $l = 0, 1, 2, 3$; a state of the electron in an atom, with its shape.
- **Spectrum.** The light sorted by wavelength; an atom's is a set of sharp lines matching the differences of its levels.
- **Magnetic moment; Bohr magneton; g-factor.** How strong a small magnet a body is, measured by the turning push a magnetic field of a given strength gives it; $e\hbar/(2m_e)$, the moment of one unit ħ of orbital angular momentum; the ratio of a particle's magnetic moment to the value its angular momentum alone would give, 2 for the electron's spin.
- **Spin-orbit coupling; fine structure.** The meeting of an electron's spin magnet with the magnetic field it finds, seen from the moving electron itself, from its motion through the electric field around it; the splitting of each energy level into a few close ones that it makes.

- **Atomic number; shell; subshell; closed subshell.** The number Z of a nucleus's protons; a set of levels of nearly the same energy with a gap above it, in an atom the states of one n, which take $2n^2$ electrons; the part of a shell with one value of l, which takes $2(2l + 1)$; a subshell with every one of its states taken.
- **Screening; effective nuclear charge.** Charges which gather round a charge and cancel its field at a distance; the true charge Z less the part the electrons between hide.
- **Madelung's rule.** With screening, the subshells fill roughly in order of $n + l$, and, at a tie, lower n first; it gives periods of 2, 8, 8, 18, 18, 32 and 32.
- **Groups and families.** The columns of the periodic table: the alkali metals and the alkaline earth metals, with one and two outer electrons; the halogens, one short of a closed p subshell; the noble gases, with their last subshell closed; the transition metals, lanthanides and actinides, in which an inner subshell fills.
- **Ionization energy; electron affinity; valence electrons.** The energy that must be supplied to free an atom's most loosely held electron; the energy set free when a neutral atom takes one more electron; the electrons beyond an atom's last closed subshell.
- **Hund's first rule.** A partly filled subshell fills with spins aligned first, because aligned electrons keep apart, screen each other less and are held more strongly; such atoms are magnets.
- **Interference; bonding state; antibonding state.** The adding of waves, which reinforce where they have the same sign and cancel where opposite; the lower state of an electron shared by two atoms; the higher one, raised more than the lower is lowered.
- **Bond; bond length; valence; lone pair.** Two atoms held together by electrons in a lower shared state; the separation of least energy; the number of electron-pair bonds an atom forms, the smaller of two numbers, its outer electrons and the electrons it lacks to complete its subshell; a pair of an atom's outer electrons that takes no part in its bonds.

- **Covalent bond; polar bond.** A bond made by a pair of electrons shared between two atoms; a covalent bond whose shared pair sits nearer one atom than the other.
- **Ionic bond; ion.** An electron passed over entirely, the two ions held by the electric pull alone, without direction; an atom or nucleus with a net charge.
- **Metallic bond.** Each atom gives its few loosely held outer electrons to be shared with all its neighbors at once, so the shared electrons move through the whole piece of metal and the bond has no direction.
- **Dispersion force; hydrogen bond.** The weak pull between all atoms and molecules from their passing separations of charge, each inducing a matching one in the other; the attraction between a hydrogen atom bound to a strongly electron-pulling atom and a lone pair of another such atom, stronger than the dispersion force and weaker than a covalent bond.
- **Isotope; zero-point energy.** Different forms of one element, with the same number of protons and different numbers of neutrons; the least energy of a vibration, half a quantum, which no cold takes away.
- **Mass number; proton number; neutron number.** The number of nucleons in a nucleus; the number of its protons, which is its charge and the atomic number of its element; the number of its neutrons, with $A = Z + N$.
- **Repulsive core.** The push between nucleons pressed closer than about half a femtometer.
- **Fusion and fission.** The joining of light nuclei into a heavier one, and the splitting of a heavy nucleus into lighter ones; both set energy free, since the binding for each nucleon peaks near iron and nickel.
- **Deuteron; alpha particle; magic numbers.** The nucleus of a proton and a neutron, of spin one, the only bound pair of nucleons; the helium-4 nucleus; the numbers of nucleons of one kind, 2, 8, 20, 28, 50, 82 and 126, at which a nuclear shell closes.

- **Spin of a nucleus.** The sum of its nucleons' spins and orbital angular momenta, taken as one: zero when every nucleon is paired, an odd number of halves when the mass number is odd, a whole number when both counts are odd.
- **Nuclear magneton.** The moment of one unit ħ of orbital angular momentum carried by a charge e with the proton's mass, 1/1836 of the Bohr magneton; the natural unit of a nucleus's magnetic moment.
- **Beta decay; gamma ray.** The turning of a neutron of a nucleus into a proton, or a proton into a neutron, by the weak force, with an electron or a positron and a neutrino given off; light of very high energy, given off when a nucleus falls to a lower state.
- **Neutron star.** A body about as massive as the Sun, or more, packed to the density of a nucleus and made mostly of neutrons, the collapsed core of a massive star.



Chapter 2

The Counting of Ways

CHAPTER OVERVIEW

A system of many particles keeps its total energy, and it has a vast number of microstates, complete arrangements of its particles, with that total. A measurement that registers only the kept totals cannot tell those microstates apart, and the system's own motion carries them into one another while keeping their weight, the probability each carries. The only weight available among them is the one the motion keeps, which gives each the same. And a preference that no measurement can register is no preference, by the principle of identity, by which what no comparison can distinguish is one thing and not two. So every microstate with the system's totals counts alike, and that is the postulate on which *statistical mechanics*, the physics of many particles built by counting their microstates, rests. The entropy of the system is the logarithm of the number of its microstates, the measure of their number that adds when independent systems are taken together. Almost all microstates lie in arrangements near the one of greatest entropy, and each arrangement with appreciably less entropy for each particle is outnumbered, by the arrangements near the greatest entropy taken together, by a factor that grows as an exponential of the number of particles. As the particles interact, each comes to carry a trace of the others, a mark in its own state of what the others were. Where those traces leave the system, as light does, they are out of reach, and the entropy of the system together with what left it does not fall. Where the system is isolated, a return would need its traces gathered back from

among more and more particles, and for many particles it is never found. The rule that the entropy does not fall is the second law, the direction of time that the count shows. Change slow enough for the system to stay in balance keeps the entropy, and faster change raises it. Temperature is the energy it takes to raise a system's entropy by one unit, so energy flows from hotter to colder, and the Boltzmann constant is a unit, not a new constant of nature. A small part of a large system is found in each of its states with a weight that falls as the exponential of the state's energy over the temperature (Box 2.3). From that weight come the partition function, the sum of the weights of all the states, and equipartition, the even sharing of energy among the ways a molecule can move. From it come too the speeds of the molecules of a gas, Saha's rule for how far atoms come apart into ions and electrons (Box 2.4), and the two kinds of filling, of fermions one to a state and of bosons any number to a state (Box 2.5). Light in a box follows the second kind with nothing fixing its number, and its energy goes as the fourth power of the temperature, three powers from the three dimensions of space and one from the photon's energy being proportional to its momentum (Box 2.6). A system held at a fixed temperature settles where its energy less its temperature times its entropy is least, so order usually wins when cold and disorder when warm. The change between them is sharp, at one temperature, only where a symmetry or a jump separates the two arrangements, and otherwise it is a smooth crossover. At the lowest temperature the entropy is the logarithm of the number of ground states, zero if there is only one.

I. So Many at Once

Chapter 1 ended with a question: a glass of water holds about 10^{25} molecules, so how can anything be said about so many? A *mole* is 6.02214076 $\times$ 10^{23} molecules, the *Avogadro constant*, exact by the definition of the mole, and a mole of water weighs 18.015 grams, its molar mass. So a glass holding 250 grams of water holds 250/18.015 moles of it, 8.4 $\times$ 10^{24} molecules. Each of them moves, turns and shakes, and each strikes its neigh-

bors many times in every billionth of a second. A thermometer dipped in the glass reads one number, and that one number is what is needed, though no one could follow the molecules one by one.

The same need was met at the end of Volume One. Volume One, Chapter 11, showed that atoms join into molecules by sharing pairs of electrons between them, the chemical bond. It showed too that how fast bonds rearrange, and every property of many particles moving at once (melting, boiling, the change between ordered and disordered arrangements), needs a counting of the ways a collection of particles can hold a given energy and of how it shares that energy among its parts. In this chapter I make that counting.

Shake a hundred coins in a cup and pour them out on a table. A glance tells you about how many show heads: roughly half. It does not tell you which ones. Pour them again, and again roughly half show heads, but almost certainly not the same coins. There are 2^{100} ways the hundred coins can fall, about 1.27×10^{30}, and the glance sees only one number, the count of heads.

A glass of water is the same in kind, with far more parts. A *many-body system* is many particles taken together, with their total energy kept: the total stays the same however the particles exchange energy among themselves, as long as nothing enters or leaves. A *microstate* of the system is one complete arrangement of it, every particle's state given. For the coins, a microstate says which coins show heads. A *macrostate* is what is found of the system as a whole: its total energy, its number of particles, the room it fills, and the other totals that every change within it keeps. For the coins, the macrostate is the number of heads.

A measurement that registers the total energy, and the few other totals the system keeps, registers nothing that tells the microstates with those totals apart. And the system's own motion carries its microstates into one another. In quantum mechanics that motion is *unitary*, a change that keeps the total weight of the possibilities, the weight of a possibility being the probability of finding it. In the words of *The Quantum Passage*, Chapter 1,

Section I, "Unitarity preserves inner products, and therefore preserves probabilities", inner products being the overlaps of states from which the probabilities are computed. The same book, Chapter 6, Section VI, derives that the motion has this form. So a glass of water at rest on a table is, at every moment, in one of a vast number of microstates, all with the same totals, which no measurement of those totals tells apart, and which its motion carries into one another while keeping their weight.

Yet the water has a temperature, and if it is warmer than the room it cools until it matches the room, and it never warms itself again from the room. So the reader's question is this: what are temperature and entropy (entropy being, in everyday words, how disordered a thing is, which Section III makes exact), and why does heat flow only one way?

II. Every Microstate Counts Alike

Why does a fair die show each face one time in six? Its six faces are alike in every way but their spots, and nothing in the throw registers the spots: the table, the air and the hand act on the die's shape and weight, which are the same for every face. A throw cannot prefer a face that nothing in it can tell from the others, and so no face comes up more often than another.

The microstates of a many-body system stand to one another as the faces of the die do, and the argument that they count alike runs in three steps.

The first step is that the system's motion carries its microstates into one another while keeping their weight (Section I).

The second step is that, among states that the motion carries into one another, the only measure of the weight of those states that is available is the measure that the motion keeps. Picture water poured from cup to cup, where every pouring moves the whole of one cup into the next and spills nothing. If one cup held more than another, the pouring would carry the excess along, and the amounts would not stay as they were. In the same way the motion carries one microstate into another and keeps how much

weight is carried. So a weighting that the motion leaves as it was must give the same weight to any two microstates that the motion carries one into the other: the measure the motion keeps gives every such microstate the same weight (mathematics).

The third step is the *principle of identity*, which *The Quantum Passage*, Chapter 8, Section VI, states so: "The principle of identity says that what no comparison can distinguish, in any way at all, even in principle, is one thing and not two". *Measurement*, Chapter 11, Section IV, states it for differences: "a difference that no comparison can register is no difference". A preference of the system for some of its microstates over others would be a difference that no measurement registers, since a measurement registers only the totals and those are the same for all of them. By the principle of identity that preference is none.

So every microstate with the system's totals counts alike. The result that every microstate counts alike is the postulate of *equal a priori probabilities*, the statement that every microstate with the given totals has the same probability. *Statistical mechanics*, the physics of many-body systems built by counting the microstates of those systems, rests on the postulate of equal a priori probabilities. Ludwig Boltzmann and Josiah Willard Gibbs took it as the starting point of the subject (Boltzmann, 1877; Gibbs, 1902). It follows by the three steps from two things already in hand: the weight the motion keeps, and the principle of identity. Every result of this chapter rests on it.

The derivation also says over which microstates the counting is made. Suppose some measurement can register a difference among microstates that share the system's totals, so that it gives some of them more weight than others. Then that difference is found, the microstates it separates are not states that no measurement tells apart, and the count is made among fewer of them. An extra kept total makes a difference of that kind among the microstates, and so the count is made among fewer microstates. A star alone in space keeps its total angular momentum as well as its energy, and a measurement of its turning registers which value it has. So its micro-

states are counted only among those with that energy and that angular momentum together. Each total that the system keeps, and that a measurement can register, narrows the set of microstates that count alike.

The equal counting holds over the whole set of microstates with the given energy, whether or not the motion joins every pair of them. The kept energy gives closure: the motion never carries a microstate with the given energy to one with another energy, so the set of microstates with that energy is kept by the motion. Within each part of the set that the motion does join, the measure the motion keeps weighs every microstate the same (the second step). Across the parts, a preference of one part over another would be a difference that no measurement registers, and by the principle of identity it is none, so the equal counting extends over every part. Where some measurement does register which part the system is in, that is an extra total that is found, and the count is made within that part. Boltzmann's own route took a stronger statement as its starting point, that the motion passes through every microstate with the given energy in time, which is called the *ergodic hypothesis*; by the three steps above, equal counting follows from closure alone.

Physicists reach much of the same result by a second route, and two routes resting on different premises that meet on one rule are a check of that rule. The second route starts from the way a small part of a large quantum system becomes *entangled* with the rest of it, its state tied to the state of the rest so that neither can be given alone. The state of the part is then the same as if every microstate of the whole counted alike. That route is called canonical typicality (Goldstein, Lebowitz, Tumulka and Zanghì, 2006; Popescu, Short and Winter, 2006), and its companion for single states of an isolated system is the eigenstate thermalization of Joshua Deutsch and Mark Srednicki (Deutsch, 1991; Srednicki, 1994).

III. Entropy, the Logarithm of the Count

A bicycle lock with one dial of ten digits can be set in ten ways. A lock with two such dials can be set in a hundred, and one with three in a thousand. Each added dial multiplies the number of settings by ten, and it adds one digit to the number written out. Join two locks, one of three dials and one of two, and the settings of the pair number a thousand times a hundred, a hundred thousand: the numbers of settings multiply, and the numbers of digits add, three and two to five.

How can the number of microstates of a glass of water be written, when it is far too large to write out? The microstates of a many-body system can be counted in the same way as the settings of the lock. They come in definite steps, as the levels of the hydrogen atom do (Volume One, Chapter 7, showed those levels separate, because a bound wave must close on itself), and so within any bounded system there is a definite number of them with a given energy. Write that number W. Two systems that do not act on each other have, together, the product of their numbers: each microstate of the first can go with each microstate of the second. A measure of how many microstates there are that adds when independent systems are taken together is therefore the logarithm of the number, as the number of digits is for the lock. The *logarithm* of a number is the power to which a fixed base must be raised to give the number: the logarithm to the base ten of a thousand is three, the count of its zeros. The logarithm turns products into sums, and up to the choice of its base it is the only smooth measure that does (mathematics).

The *entropy* of a system is the logarithm of the number of its microstates with its totals, the microstates that no available measurement tells apart:

$S = k \ln W,$

where ln is the natural logarithm, the logarithm to the base e = 2.718, and k is the Boltzmann constant, a unit that Section VIII explains. Boltzmann found the relation between entropy and the count (Boltzmann, 1877). Entropy is a count, made small enough to write by taking its logarithm. *The Coming of the Kinds*, Chapter 2, gives it in the same sense, quoting *At the Edge of Reality*: entropy is "a count: the number of states that a context can distinguish", that is, the number of states that the setting of a measurement can tell apart. The same book adds, "High entropy is disorder in the everyday sense: many ways for things to be, all looking alike from outside".

Two counts must be kept apart here, since in Section VI we meet the count of states of a kind of particle in *The Coming of the Kinds*, Chapter 10, which keeps the two apart. The *count of states* of a kind of particle, in that book's Chapter 3, is the number of distinct ways one particle of that kind can be, apart from where it is and how it moves: the photon has two, for its two senses of turning. The entropy of a system counts the arrangements of the whole system, every particle at once. The count of states is a property of one particle, and it helps set how much entropy a system of such particles has at a given temperature. The entropy is a property of the whole.

Box 2.1 makes the counting concrete for a simple solid, in which each atom is a small spring that can hold energy only in whole quanta.

Box 2.1. A worked count: quanta shared among springs

Premises. (1) A solid is taken as N oscillators, each an atom bound to its place as if by a spring, each holding energy in whole quanta of one size, hf, with f the oscillator's frequency and h Planck's constant (the model of Einstein, 1907; standard quantum mechanics). (2) A microstate says how many quanta each oscillator holds; a macrostate gives only N and the total number of quanta, q. (3) The number of ways to share q like quanta among N oscillators is $W(N, q) = (q + N - 1)!/(q!(N - 1)!)$, where n! is the product $1 \times 2 \times ... \times n$: the number of ways to set q marks and $N - 1$

partitions in a row (mathematics). (4) Stirling's approximation: for large n, ln n! is close to n ln n − n, and its share of error falls as n grows (mathematics).

Steps. For N = 3 and q = 3, W = 5!/(3! 2!) = 10: the three quanta can sit (3, 0, 0) in three ways, (2, 1, 0) in six and (1, 1, 1) in one. For N = 500 and q = 100, W = 599!/(100! 499!) = 9.26×10^{115}, and ln W = 267.0. By (4), ln W is close to (q + N) ln(q + N) − q ln q − N ln N = 600 ln 600 − 100 ln 100 − 500 ln 500 = 270.3, within about one part in eighty of the exact value; the difference grows only as the logarithm of N while ln W grows in proportion to N, so for a solid of 10^{24} atoms the approximation is exact to every figure that matters.

Result. Five hundred springs sharing a hundred quanta already have about 10^{116} microstates, and their entropy, the logarithm, is about 267 in units of k. The count grows as an exponential of the number of particles, and its logarithm, the entropy, grows in proportion to the number of particles: entropy adds as the system grows, as the digits of the lock do.

IV. Almost All States Lie Near the Greatest Entropy

Where, among all its microstates, is a system to be found? Go back to the hundred coins. Of their 1.27×10^{30} arrangements, the arrangements with exactly fifty heads are the most numerous of any count of heads, about 10^{29} of them. Yet they are only 8.0 percent of all arrangements. The arrangements with between forty and sixty heads are 96.5 percent of all. And the two arrangements with every coin the same, all heads or all tails, are each one arrangement among 1.27×10^{30}. Almost all arrangements lie near half heads, though no single count of heads holds most of them.

The same holds in every many-body system. Of all the microstates with a given energy, almost all lie in macrostates near the macrostate of greatest entropy. Each macrostate whose entropy for each particle is appreciably less is outnumbered, by the macrostates near the greatest entropy taken together, by a factor that grows as an exponential of the num-

ber of particles (mathematics). The single macrostate of greatest entropy holds only a small share of the microstates, of order one over the square root of the number of particles. What holds almost all of them is the narrow band of macrostates near it.

Take the springs of Box 2.1 as two solids side by side, one of 300 springs and one of 200, sharing 100 quanta between them, so that together they are the 500 springs of the box. For each way of dividing the quanta, the number of microstates of the pair is the number for the first solid times the number for the second. The division with the most microstates puts 60 quanta in the first solid and 40 in the second, in proportion to their sizes, a fifth of a quantum for each spring in both. That one division holds 7.4 percent of all the microstates of the pair, and the divisions from 50 to 70 quanta in the first solid hold 95 percent. The division with every quantum in the second solid holds a share of 3.0×10^{-35}. Every division with 30 quanta or fewer in the first solid holds, all together, a share of 2.7×10^{-8} (computed with the count of Box 2.1, premise 3).

The band near the greatest entropy narrows as the system grows. For coins, the typical departure of the fraction of heads from one half is one over twice the square root of the number of coins: 0.16 for ten coins, 0.05 for a hundred, 0.016 for a thousand, and 5×10^{-13} for 10^{24} (mathematics, from the count of arrangements). Figure 2.1 draws the count for ten, a hundred and a thousand coins.

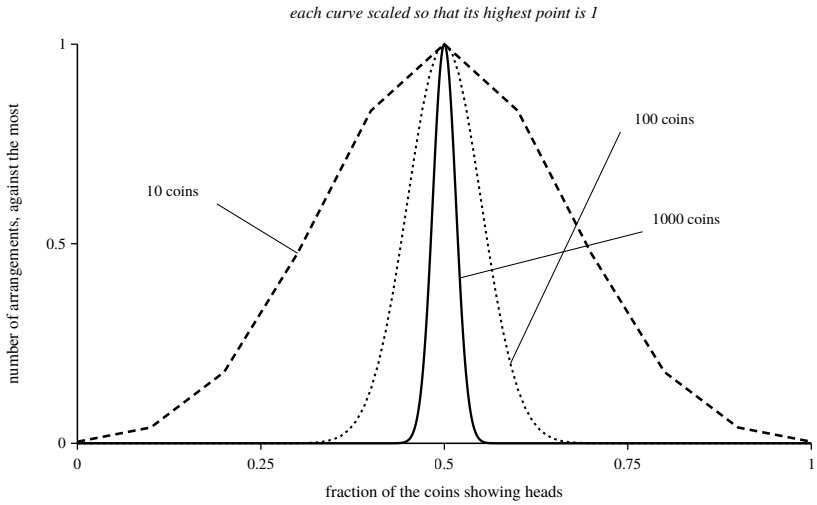


Figure 2.1. The number of arrangements of N coins with each fraction of heads, for 10, 100 and 1000 coins, each curve scaled so that its highest point, at half heads, is 1; computed exactly from the count of arrangements. The curves narrow as the number of coins grows: a curve stands at half its peak or higher only for fractions of heads from 0.40 to 0.60 for 10 coins, from 0.45 to 0.55 for 100, and from 0.482 to 0.518 for 1000. For the 10^{24} molecules of a glass of water the curve would be far too narrow to draw.

Such departures are the *fluctuations* of a system: the small, ever-changing differences of its macrostate from the most probable one, which the motion of its particles makes. Their size, against the whole, goes as one over the square root of the number of particles. In a glass of water they are far too small to find with a thermometer, and that is why the results of this chapter are sharp for anything that can be held in the hand. In a system of a few hundred particles they are large enough to see, and the results of this chapter hold there as averages, with scatter about them of the size the count gives.

V. Why Entropy Does Not Fall

Let a drop of ink fall into a still glass of water. It drifts out in curling threads, the threads thin, and in an hour the whole glass is faintly and evenly tinted. No one has ever seen the tint gather itself back into a drop.

Section IV says where the ink is going: toward the macrostates of greatest entropy, which hold almost all the microstates, since an evenly tinted glass can be arranged in vastly more ways than a glass with all the ink in one place. It does not yet say why the ink never comes back. The motion of the molecules keeps weight and can be run either way in time. For every motion that scatters the ink through the glass there is a reversed motion that gathers it. Why is the reversed one never found?

The reason lies in what interacting particles do to one another. A particle can be in several states at once, its alternatives, each with its own weight, and its alternatives combine as waves do. Where their waves meet in step they reinforce, and where they meet out of step they cancel, as the waves of the two loudspeakers of Chapter 1, Section VIII, did. How far each alternative stands ahead of another in its swing is a relation of phase between them, phase being used here in the wave's sense (The Ladder in Brief), and these relations of phase are what let the alternatives combine and interfere. When two particles strike, each is changed in a way that depends on the other's state, so each comes to carry a trace of the other: from then on, the state of the one is tied to the state of the other. The relations of phase among one particle's alternatives then pass into the joint state of the two, and they are no longer found in that particle alone. This passing is called *decoherence*. *The Quantum Passage*, Chapter 9, Section VI, follows it: as the surroundings interact with a system, the terms that carry those relations of phase become part of the joint system and are "no longer attributable to the subsystem alone" (also Zurek, 2003). A return of the ink to

its drop would need every such trace gathered back and the relations of phase restored. Whether that can be done depends on where the traces have gone, and there are two cases.

The first case is a system open to its surroundings, which is every real system. Some of the traces leave it. A warm glass of water sends out light, and light that has left travels away at the speed of light and cannot be called back. The traces it carries are out of reach: no measurement that can be made on the system and its neighborhood can gather them again. So the system cannot return to an arrangement of less entropy by gathering back what it has given out, and the entropy of the system together with what has left it never falls, with no exception.

The second case is a system wholly isolated, from which nothing leaves. Its traces stay within reach in principle, among its own particles, and a measurement could in principle gather them and restore the relations of phase. But the difficulty of doing so grows as the traces reach more particles. To undo the scattering of the ink, a measurement would have to act on every particle that the traces have reached, and restore the relations among all of their joint alternatives together. The number of those joint alternatives grows as an exponential of the number of particles the traces have reached (Section IV). So the share of the system's microstates from which its motion leads back to the drop is smaller than any measurement could pick out, by a factor that grows as an exponential of that number. A return is found only where the traces have reached few particles, and never where they have reached many.

The return among few has been found, and how it was found shows why it is found only there. Picture runners on a track who start together from one line at a pistol shot, each at a speed of his own. After a minute they are strung out round the track. At a second shot each turns and runs back at his own speed, and after another minute they all arrive at the starting line together. The scattering of the runners was undone, because each runner carried the trace of how far he had pulled ahead or fallen behind in his own place on the track, and one shot reversed every runner at once.

Erwin Hahn did this with the nuclei of atoms in a liquid (Hahn, 1950). Each nucleus has a spin, angular momentum carried in itself, and with it is a small magnet, and in a magnetic field its spin turns about the field's direction. Nuclei in slightly different fields turn at slightly different rates, so a set of them lined up together soon drifts out of step, and the signal they give together dies away. A first pulse of radio waves tips the nuclei so that they turn together. After they have drifted out of step, a second pulse reverses the sense of each nucleus's drift, so that each now runs back toward the others, and after a further equal time their signal returns: the *spin echo* (Hahn, 1950). Hahn's second pulse turned the spins through a right angle; the form in which the second pulse turns every nucleus over, through a half turn, is the one that Herman Carr and Edward Purcell used (Carr and Purcell, 1954). The echo comes back because the drift was held in each nucleus's own angle, one trace for each nucleus, which one pulse could reverse. Won-Kyu Rhim, Alexander Pines and John Waugh later reversed even the nuclei's interactions with one another (Rhim, Pines and Waugh, 1971). Each such reversal acts on the traces that the motion has made among the particles a pulse can reach. No reversal gathers back the traces that a warm body's light or a glass of water's collisions carry to countless particles, for the reason the count gives.

So the entropy of a system does not fall, in two cases. For a system open to its surroundings, counting what has left it, it never falls, with no exception. For an isolated system of many particles it does not fall because a return would need traces gathered back from among a number of alternatives that grows as an exponential of the number of particles, and such a return is never found. The *second law of thermodynamics* is that the entropy of an isolated system does not decrease.

VI. The Arrow of Time, and Change Slow and Fast

Run a film of the ink backward, and it looks wrong at once: threads of tint gather out of clear water into a drop. Run a film of one swinging pendulum backward, and nothing looks wrong (Volume One, Chapter 7, used that picture for the reversal of time in the atom's motion). What tells the direction of the film is the count.

The second law is the *thermodynamic arrow of time*: the direction of time that the count shows. *Measurement*, Chapter 12, Section VII, sets out how it is related to a second direction of time, which every single act of finding has. That direction is "read from the order of acts", an act being one act of comparison, such as a measurement: every record follows the act it records, and "It is present in every single comparison". The direction of the count is "the growth of entropy in an isolated system, which thermodynamics finds", a direction found "in systems of very many parts". The same section joins them: "Every record follows the act it records, and so does every increase of entropy that a record registers", and "each act of recording joins the two arrows in one event". A trace becomes a record, a finding that is not undone, when it is held by something that keeps it, something large enough that the small jostlings of its parts do not undo it (Chapter 8, Section IV). *The Basis of Physics*, Essay 11, places the order of acts beneath the growth of entropy, as "a non-entropic temporal asymmetry" that the Incommensuration Theorem requires: a one-way order in time that does not come from entropy. In Section V we found the second law in the traces the particles make of one another: once they have reached many particles, they stay, and their staying, counted over the microstates, is the growth of entropy. So the arrow of the count is the order in which every trace follows the act that makes it, counted over very many particles.

That the entropy does not fall leaves two ways for it to go: it can stay the same, or it can rise. Which it does depends on how fast a change is made.

Take a gas in one half of a box, held there by a thin wall, with the other half empty. Burst the wall, and the gas rushes into the whole box. It does no work on anything, and its energy is the same afterward. But every molecule now has twice the room, so the number of places open to each molecule has doubled, and the number of microstates of the gas has been multiplied by 2 for each molecule, by 2^N for N molecules. The entropy has risen by N k ln 2. Now take the same gas in the same half box, and instead of bursting the wall, move it slowly outward, as a piston, letting the gas push it. The gas does work on the piston and gives up energy as it does, and with less energy each molecule has fewer ways to move. The gain in room and the loss in energy balance, and the entropy stays the same.

A system is in balance when it is in the settled state in which nothing further changes on average (Section VII). A change slow enough that the system stays in balance at every step of it is *reversible*: it can be run back the other way, through the same states, by changing the outside conditions back as slowly. A reversible change keeps the entropy. A change too fast for the system to keep up, such as the bursting wall, is *irreversible*, and it raises the entropy. *The Coming of the Kinds*, Chapter 10, uses the rule that slow change keeps the entropy: while the expansion of the universe was slow against the reactions of the hot gathering of particles and light that filled it, "it keeps that gathering's entropy". The count of states before and after the electrons and positrons annihilated gives the ratio of the temperatures of the light and the neutrinos. Slow change keeps the entropy and fast change raises it, and neither lowers the entropy of an isolated system.

VII. Temperature

A cup of hot coffee left on a table cools until it is as warm as the room, and then it stays so. A cup of cold milk left beside it warms to the same mark. The room never heats the coffee above itself, and never cools the milk below itself. What is it that the coffee, the milk and the room come to share, and why does heat flow only from the hotter to the colder?

Let two systems share energy, each able to pass energy to the other, with the total of the two kept. By Section IV they are found, ever more surely, in the division of the energy that gives the pair the most microstates, the division of greatest joint entropy. At that division, moving a small amount of energy from one system to the other gains the receiver exactly as much entropy as it costs the giver. The receiver's gain equals the giver's cost because at the top of a hill a small step either way neither climbs nor falls (mathematics: at a greatest value, the change is zero). So two systems stand still against each other when each gains the same entropy for each small amount of energy it takes in.

That rate gives temperature its meaning. Write the entropy as the pure count ln W, with no unit. The *temperature* of a system is the energy it takes to raise the system's entropy by one unit, that is, to raise the logarithm of its count by one: $T = dE/dS$, read "the change in energy over the change in entropy", or $1/T = dS/dE$. A cold system gains much entropy from a little energy, so its temperature is low. A hot system gains little entropy from the same energy, so its temperature is high. The springs of Section IV show it: at the division with the most microstates, the two solids each hold a fifth of a quantum for each spring, and two solids of the same kind holding the same energy for each spring have the same temperature.

Two results follow at once. Systems at one temperature exchange no energy on balance, since a move either way changes their joint entropy by nothing. So two systems each in balance with a third are in balance with each other, and the third can be a thermometer. The rule that two systems

each in balance with a third are in balance with each other is the *zeroth law of thermodynamics*. The *first law* is that energy is kept, its total never changing, and the second is the law of Section V. And when the temperatures differ, energy passes from the hotter to the colder, because that raises the joint entropy. An amount of energy E leaving a system at temperature T_h lowers its entropy by E/T_h, and entering a system at the lower temperature T_c raises that system's entropy by E/T_c, which is more. Energy that passes from one system to another because of a difference of temperature is *heat*. So heat flows from hotter to colder, and the reverse would lower the joint entropy, which Section V excludes.

Equilibrium, which *The Coming of the Kinds*, Chapter 2, also calls balance, is "the settled state in which nothing further changes on average", and two systems in contact reach it when their temperatures are equal. How much energy a system takes up as its temperature rises is its *heat capacity*: the energy taken up for each rise of one unit in temperature, $C = dE/dT$. Water's heat capacity is large among common liquids: liquid water at 25 degrees Celsius takes up 4.18 joules for each gram and each kelvin of rise, against 2.44 for ethanol, the alcohol of wine (computed from the measured 75.3 and 112.4 joules for each mole and each kelvin, as the NIST Chemistry WebBook gives them, from Chase, 1998, and Petrov et al., 1989). Water's large heat capacity is why a lake warms slowly in spring. Chapter 5 shows why the heat capacity of a solid falls away as it is cooled.

VIII. The Boltzmann Constant Is a Unit

A thermometer marked in degrees seems to measure something of its own kind, neither a length nor a mass nor an energy. Is temperature, then, a new kind of quantity, with a new constant of nature to go with it? The counting says it is not.

Temperature is defined as an energy for each unit of entropy, and entropy is a pure count, the logarithm of a number of microstates, which carries no unit. So temperature is measured in energy. A temperature can

be given in joules, or in electron volts, the energy an electron gains in passing through one volt. The factor that turns a temperature written in degrees into an energy is a unit chosen by those who measure: the *Boltzmann constant*, k = 1.380649 × 10^{-23} joules per kelvin, or 8.617333262 × 10^{-5} electron volts per kelvin. The *kelvin* is the unit of temperature on the scale that starts at the lowest temperature there is, with steps the size of the Celsius degree, so that water freezes at 273.15 kelvin. Joules per kelvin is the unit of the Boltzmann constant, which converts a temperature in kelvin to an energy. Since 2019 the kelvin has been defined by fixing the Boltzmann constant at exactly that value (*The Strengths of the Kinds*, Chapter 1, Section II: the kelvin is fixed "by the Boltzmann constant, 1.380649 × 10^{-23} J/K").

In energy, a room at 300 kelvin has kT = 0.0259 eV, about a fortieth of an electron volt, and one electron volt is the energy of 11,604.5 kelvin (computed with k). Wherever this volume writes kT, it means the temperature as an energy. Wherever k is set to one, as *The Coming of the Kinds* sets it, together with the reduced Planck constant and the speed of light, temperature is written directly in energy. Setting k to one is allowed precisely because the Boltzmann constant converts one unit into another and carries no fact about nature.

So temperature introduces no new constant of nature. *The Strengths of the Kinds*, Chapter 1, Section II, names four relations that do carry facts about nature: c, the speed of light; ħ; α, the strength of electromagnetism; and G, Newton's constant of gravitation. Each is called a relation because it relates two of the ideas by which things are compared and found, as c relates space to time. That book counts the unit of temperature among the units and conventions that "add no kind of magnitude", so the four relations remain the complete set, and the Boltzmann constant is not a fifth. So every temperature in this volume can be set beside every energy of the ladder: written as kT, a temperature is an energy.

IX. Heat, Work and the Limit of an Engine

A steam engine burns coal to boil water, the steam drives a piston, and the spent steam is cooled and condensed. The engine turns heat into motion, and it always gives some heat away to the cold side: every engine ever built has turned only part of the heat it took in into motion.

Work is energy passed by a force that moves something along its way, as the steam pushes the piston. Work moves the piston as a whole, in one way, and it adds no microstates to anything, so it carries no entropy with it. Heat carries entropy: heat E taken from a body at temperature T takes entropy E/T with it (Section VII). An engine that runs in a cycle comes back to its own starting state each time round, so over each cycle it keeps no entropy of its own. The entropy it takes in with the heat from the hot side must go somewhere, and work cannot carry it, so the engine must give heat to a cold side. Sadi Carnot found the limit this sets (Carnot, 1824), and Box 2.2 derives it from the entropy.

Box 2.2. Carnot's limit

Premises. (1) An engine runs in a cycle, returning to its own starting state, so over a cycle its own energy and entropy are unchanged. (2) In each cycle it takes heat Q_h from a hot body at temperature T_h, gives heat Q_c to a cold body at temperature T_c, and gives out work W; by the keeping of energy, $W = Q_h - Q_c$. (3) Heat Q leaving or entering a body at temperature T carries entropy Q/T; work carries none (Section VII and this section). (4) The entropy of the engine with the two bodies does not fall (Section V).

Steps. Over a cycle the hot body loses entropy Q_h/T_h, the cold body gains Q_c/T_c, and the engine's is unchanged by (1). By (4), $Q_c/T_c \geq Q_h/T_h$, so $Q_c \geq Q_h T_c/T_h$. By (2), $W/Q_h = 1 - Q_c/Q_h \leq 1 - T_c/T_h$. The equality holds for an engine every step of which is reversible (Section VI). Run backward, the same cycle uses work W to move heat Q_c out of the cold

body and give Q_h to the hot one; then $Q_c/W \leq T_c/(T_h - T_c)$ for a refrigerator, which counts the heat it takes out, and $Q_h/W \leq T_h/(T_h - T_c)$ for a heat pump, which counts the heat it delivers.

Result. No engine working between temperatures T_h and T_c, in kelvin, turns more than a share $1 - T_c/T_h$ of the heat it takes in into work: an engine taking heat at 600 kelvin and giving it up at 300 kelvin turns at most half. A heat pump warming a room at 293.15 kelvin (20 degrees Celsius) from outdoor air at 273.15 kelvin (0 degrees) can deliver at most 14.7 times the work it uses as heat to the room.

The limit belongs to the temperatures alone, not to steam or to any other working substance, because it comes from counting entropy.

Could a device clever enough to sort the molecules get round the limit? James Clerk Maxwell pictured a being at a small door in a wall between two halves of a box of gas, a being who can follow every molecule and who opens the door only to let the faster molecules pass one way and the slower ones the other (Maxwell, 1871). With no work done, one half warms and the other cools, and the entropy of the gas falls. Such a sorter must find out, molecule by molecule, how each one moves, and it must keep each finding until it acts on it, as Leo Szilard saw (Szilard, 1929).

A finding is kept in a *memory*: a small system that can stand in any of several states, one for each finding it can keep. A memory of two states keeps one *bit*, the smallest piece of information, one choice between two (Chapter 8, In Use). Before the finding the memory stands in its one blank state, and after it in one of its two states, so the count of its microstates has doubled and its entropy has risen by k ln 2. The gas, the sorter and its memory together keep the rule of Section V: their entropy, counted with whatever leaves them, does not fall. So the sorting can take from the gas no more entropy than the memory gains, k ln 2 for each bit it keeps. Writ-

ing a finding into a blank memory can itself be done reversibly, in the sense of Section VI, at no cost of work: in Charles Bennett's words, the measurement “in principle can be done reversibly” (Bennett, 1982).

The heat is given off when the memory is cleared. A sorter that goes on working must clear its memory to make room for the next finding, and clearing sets the memory to its one blank state, whatever it held, which halves the count of its microstates for each bit. The entropy of everything together does not fall, so the surroundings must gain at least k ln 2 for each bit cleared, and at temperature T that is heat of at least kT ln 2 given off for each bit (Landauer, 1961). At room temperature, 300 kelvin, that is 0.0179 eV, or 2.87×10^{-21} joules, for each bit (computed with k). Antoine Bérut and his colleagues made a memory of one bit from a bead of silica two micrometers across, held by laser light in either of two hollows of energy side by side, and found that when the clearing is made slow “the mean dissipated heat does saturate at the Landauer limit”, the kT ln 2 for each bit (Bérut, Arakelyan, Petrosyan, Ciliberto, Dillenschneider and Lutz, 2012). So the entropy that a sorter takes from the gas is given back to the surroundings, at least in full, when the sorter clears its memory, and no sorter lowers the entropy of everything together.

So we now know why heat flows one way and why no engine turns all its heat to work: both are the second law, the entropy that does not fall, applied to energy passing between bodies at different temperatures.

X. A Small Part of a Large Whole

Climb a high mountain and the air thins: each breath holds fewer molecules than it did in the valley. A molecule high on the mountain holds more energy, against the pull of gravity, than one in the valley, and fewer molecules are found up there. The atmosphere is a large system, and each molecule in it is a small part. How often is a small part of a large system found holding a given energy?

Take a small part, a single molecule or a single atom, in contact with a large system at some temperature, the two together keeping their total energy. If the part holds an amount of energy, the large system holds the rest, and the number of ways the large system can hold the rest is smaller by a factor that falls as the exponential of that amount over the temperature. Every microstate of the two together counts alike (Section II), so the part is found in each of its states with a weight in proportion to the number of microstates the large system then has. So the part is found in a state of energy E with a weight $e^{-E/kT}$, the *Boltzmann factor*, read "e to the minus E over kT". Box 2.3 carries the derivation.

Box 2.3. The Boltzmann factor from counting

Premises. (1) A small part P is in contact with a large system R, and the two keep their total energy E_{tot}. (2) Every microstate of P and R together with the total E_{tot} counts alike (Section II). (3) The entropy of R, S_R, is the logarithm of its number of microstates W_R, and it changes with R's energy at the rate $dS_R/dE = 1/(kT)$, with T the temperature of R (Sections III, VII and VIII, the entropy written as a pure count). (4) The energies the part can hold are small against R's: a change in R's energy of that size changes R's temperature by a share smaller than any that matters.

Steps. Fix one state i of the part, with energy E_i. Then R holds $E_{tot} - E_i$, and the number of microstates of the whole with the part in state i is $W_R(E_{tot} - E_i) = \exp[S_R(E_{tot} - E_i)]$. By (3) and (4), $S_R(E_{tot} - E_i) = S_R(E_{tot}) - E_i/(kT)$, the next term being smaller than this one by the share of (4). So that number is $\exp[S_R(E_{tot})] \times e^{-E_i/kT}$, and the first factor is the same for every state of the part. By (2), the probability of state i is in proportion to that number: $P_i = e^{-E_i/kT}/Z$, with $Z = \Sigma_j\, e^{-E_j/kT}$, the sum over every state j of the part, so that the probabilities add to one.

Result. A small part of a large system at temperature T is found in a state of energy E with probability in proportion to $e^{-E/kT}$. A state that holds kT more energy than another is found $e = 2.718$ times less often; a state that holds ten times kT more is found 22,000 times less often.

The sum Z of Box 2.3 is the *partition function*: the sum of the Boltzmann factors of all the states of the part. It is a working tool. The share of parts in any one state is that state's factor over Z. The average energy, the heat capacity and the free energy all come from Z by a few lines of calculus, the free energy being the share of a system's energy that can be drawn off as work (Section XIV). States that share one energy count separately in it, so a level of g states enters with weight $g\,e^{-E/kT}$.

Hydrogen shows how strongly the factor works. Its level $n = 2$ lies 10.2 eV above its ground state, the state of least energy it can have, and has 8 states against the ground state's 2 (Volume One, Chapter 7, counted $2n^2$ states, with spin, in level n). At room temperature, 300 kelvin, kT is 0.02585 eV unrounded, and the share of hydrogen atoms in level 2 against level 1 is $4\,e^{-10.2/0.02585}$, about 2×10^{-171} (computed): not one atom in all the hydrogen there is. At the Sun's surface, 5772 kelvin (International Astronomical Union, 2015, nominal value; Prša et al., 2016), kT is 0.497 eV and the share is 5×10^{-9}. The share at the Sun's surface is enough for the Sun's hydrogen to take in the Balmer lines, and the Balmer lines are seen as dark lines in sunlight. The Balmer lines are the lines of visible light that hydrogen takes in when hydrogen's electron is lifted from level 2. *The Coming of the Kinds*, Chapter 3, uses the same factor for the early universe, where particles were made in pairs: a kind whose mass lies well above the temperature is present in numbers that fall as $\exp(-m/T)$, its mass written as an energy and the temperature in energy. So the factor that thins the air on a mountain also thinned out the heavy particles as the early universe cooled.

Two results follow for motion. The first result for motion is *equipartition*. An energy that goes as the square of a position or of a velocity, such as the energy of motion $\frac{1}{2}mv^2$ along one direction or the energy of a stretched spring, holds on average $\frac{1}{2}kT$, whatever the mass or the stiffness, when kT is large against the size of the quanta of that motion (mathematics, from the Boltzmann factor). So an atom of a gas, free to move in three directions, holds on average 3/2 kT of energy of motion, 0.039 eV at 300 kelvin. A mole of such atoms takes up $3/2\ N_A k = 12.47$ joules for each kelvin of rise, its heat capacity. Each spring of a solid holds kT, half in its motion and half in its stretch. When kT is small against the quanta of a motion, the motion holds almost nothing, since even one quantum is suppressed by its Boltzmann factor: that motion is frozen out.

The second result for motion is the range of speeds among the molecules of a gas, the *Maxwell-Boltzmann distribution* (Maxwell, 1860). The weight of a speed v is the Boltzmann factor of its energy, $e^{-mv^2/2kT}$, times the number of ways of moving at that speed, which grows as v^2 because the velocities of one size fill a sphere's surface in three dimensions. For the nitrogen of air at 300 kelvin, with a molecule's mass 28.014 atomic mass units (the atomic mass unit is a twelfth of the mass of an atom of carbon-12), the most common speed is 422 meters a second and the average 476 (computed). Few molecules are slow, since few velocities are small, and few are very fast, since their factor is small. The share of molecules whose energy exceeds a given value E far above kT falls off as $e^{-E/kT}$. That last tail is the one Chapter 3 needs, because it sets how often a molecule holds enough energy to break a bond.

XI. Particles That Come and Go

At the checkout of a busy shop, shoppers leave a long line for a shorter one, and the lines settle when no shopper can gain by moving. Each move that shortens a wait is made, and the moves stop when there are none left to make, though no one tells the shoppers to make the lines equal. Where do particles settle when they, too, can come and go?

Particles do the same when they can pass from one place to another, or from one kind of binding to another. Energy passes from where the temperature is higher to where it is lower (Section VII), because that raises the joint entropy. In the same way, particles pass from one place to another wherever the move raises the joint entropy, and they settle when moving one more particle either way changes the joint entropy by nothing. The quantity that decides which way they move has a name. The *chemical potential* of a kind of particle in a system, written μ and read "mu", is the energy that adding one more particle of that kind brings to the system when its entropy and its volume are held fixed. Particles pass from where their chemical potential is higher to where it is lower, until it is equal, and then they are in balance. So, as temperature decides which way energy flows, the chemical potential decides which way particles flow.

Where particles change into one another, as in a reaction, the same rule says where the reaction settles. *The Coming of the Kinds*, Box 3.1, premise 2, states it as standard physics: "For each reaction that runs in balance, the chemical potentials of what goes in add up to those of what comes out". And it states the chemical potential of light: since a particle and its antiparticle can annihilate into two photons or three or more, no count of photons is kept, and "the chemical potential of photons vanishes in equilibrium" (premise 3). A kind whose number no change keeps has a chemical potential of zero.

For a gas thin enough that its particles seldom share a state, the chemical potential follows from the Boltzmann factor and from the count of states in a box. The number of particles of a gas in balance, for each unit of volume, is the number of states of one particle for each unit of volume, times the Boltzmann factor of each state's energy measured from μ, summed over the states. The sum gives one particle's worth for each cube of side about the particle's *thermal wavelength*, the length of the wave of a particle moving at the gas's typical speed. Box 2.4 carries the count through for the first use of it: the balance between free electrons and atoms that *The Coming of the Kinds*, Box 13.1, applied to the hydrogen of the early universe. That balance follows the rule that Meghnad Saha set out in 1920 for the gases of the Sun's outer layers (Saha, 1920).

Box 2.4. Saha's rule from the counting

Premises. (1) A particle of mass m in a box of volume V has $V\, d^3p/(2\pi\hbar)^3$ states for each of its internal states in each small range d^3p of momentum, and energy $mc^2 + p^2/(2m)$ when it moves slowly against light (standard quantum mechanics). (2) In a thin gas each state holds, on average, the Boltzmann factor $e^{-(E\,-\,\mu)/kT}$ of its energy measured from the chemical potential (Box 2.3, with particles exchanged as well as energy; Box 2.5 gives the exact form, of which this is the thin limit). (3) The integral, the sum over a continuous range, of $e^{-p^2/(2mkT)}\ d^3p$ over all momenta is $(2\pi mkT)^{3/2}$ (mathematics). (4) In balance, $e^- + p \leftrightarrow H + \gamma$, the photon's chemical potential is zero, so $\mu_e + \mu_p = \mu_H$ (this section; *The Coming of the Kinds*, Box 3.1, premises 2 and 3). (5) The electron and the proton each have 2 states of spin; the hydrogen atom in its ground state has 4, the two spins combined; at the temperatures that matter its higher levels hold a share too small to count (Section X). (6) $m_Hc^2 = m_pc^2 + m_ec^2 - B$, with $B = 13.598$ eV the binding energy of hydrogen (Volume One, Chapter 7).

Steps. By (1), (2) and (3), a kind with g internal states has, for each unit of volume, $n = g\ (mkT/(2\pi\hbar^2))^{3/2}\ e^{-(mc^2\,-\,\mu)/kT}$. Form n_en_p/n_H: by (4) the chemical potentials cancel, by (6) the rest energies leave $e^{-B/kT}$, and

by (5) the factors g give $2 \times 2/4 = 1$. The masses give $(m_e m_p/m_H)^{3/2}$, which is $m_e^{3/2}$ to within one part in a thousand. So $n_e n_p/n_H = (m_e kT/(2\pi\hbar^2))^{3/2} e^{-B/kT}$.

Result. The ratio of free electrons and protons to hydrogen atoms found above is Saha's rule, the premise that *The Coming of the Kinds*, Box 13.1, cites, written there in units where ħ, c and k are one. The rule weighs two things against each other: the binding, through $e^{-B/kT}$, which favors the atom; and the room a free electron has, through $(m_e kT/(2\pi\hbar^2))^{3/2}$, the number of states for each unit of volume open to it, which favors the free electron. The early universe held 2.2 billion photons for each hydrogen nucleus, so its hydrogen was very thin, and in a thin gas the room a free electron has outweighs the binding until kT falls far below B. So that book shows half the electrons of hydrogen bound in balance only at about 3,700 kelvin, 0.32 eV, a forty-second of the binding.

So the first use of the counting is one *The Coming of the Kinds* already made. The electrons of the early universe stayed free until the temperature fell far below hydrogen's binding, because a free electron has so many more ways to be than a bound one. Chapter 3 uses the same rule for every reaction, as the law of mass action: the rule that a reaction in balance settles where the amounts of what goes in and of what comes out stand in a fixed ratio, set by the temperature.

XII. Two Kinds of Filling

A hotel gives each guest a room of his own, and when the cheapest rooms are taken the next guest must pay for a dearer one. A campground lets any number of campers pitch their tents on one spot, and on a cold night they crowd onto the best one. How do particles fill the states open to them, when many are crowded together?

Particles fill their states in one of these two ways. A *fermion* is a particle whose spin is an odd number of halves, such as the electron, whose spin is one half. A *boson* is a particle whose spin is a whole number, such as the photon. No two fermions of one kind can share a state: this is exclusion, which follows from the principle of identity (Chapter 1, Box 1.2). Any number of bosons of one kind can share a state. The same rule holds for wholes (Chapter 1, Section IV). A whole made of an odd number of fermions, such as a proton of three quarks, is excluded as a fermion is, and a whole made of an even number, such as an atom of helium-4 with its two protons, two neutrons and two electrons, is not excluded.

So the Boltzmann factor, applied to a single state that particles can enter and leave, splits into two forms. For fermions, and wholes of an odd number of them, each state holds one particle or none, so the weight of a state being taken follows one form. For photons, other bosons and wholes of an even number of fermions, a state can hold any number, and the weight follows another. Box 2.5 derives both, from equal counting (Section II), the Boltzmann factor (Box 2.3) and exclusion. *The Coming of the Kinds*, Box 3.1, premise 1, cites the two as standard physics, and Box 2.5 gives the reason for them.

Box 2.5. The Fermi and Bose distributions

Premises. (1) One state of a single particle, with energy ε, can take in and give up particles of one kind and energy from a large system at temperature T and chemical potential μ. (2) When the state holds n particles, the large system has given up n particles and $n\varepsilon$ of energy, and its number of microstates is smaller by the factor $e^{-n(\varepsilon - \mu)/kT}$ (Box 2.3, with the definition of μ of Section XI); by Section II the weight of n is in proportion to that factor. (3) For fermions, n is 0 or 1 (exclusion); for bosons, n is 0, 1, 2, and so on, without end (this section). (4) For any $x > 0$, $1 + e^{-x} + e^{-2x} + \ldots = 1/(1 - e^{-x})$, and the sum of $n\, e^{-nx}$ over n is $e^{-x}/(1 - e^{-x})^2$ (mathematics).

Steps. Write $x = (\varepsilon - \mu)/kT$. Fermions: the weights are 1 for $n = 0$ and e^{-x} for $n = 1$, so the average number in the state is $e^{-x}/(1 + e^{-x}) = 1/(e^{x} + 1)$. Bosons: by (4), the average number is $[e^{-x}/(1 - e^{-x})^2] \times (1 - e^{-x}) = 1/(e^{x} - 1)$, which needs $x > 0$: the chemical potential of bosons lies below the lowest energy of a state. When x is large, both forms come to e^{-x}, the Boltzmann factor itself.

Result. A state of energy ε holds on average $1/(e^{(\varepsilon - \mu)/kT} + 1)$ fermions, the *Fermi-Dirac distribution* (Fermi, 1926), and $1/(e^{(\varepsilon - \mu)/kT} - 1)$ bosons, the *Bose-Einstein distribution* (Bose, 1924); where states are sparsely taken the two agree with each other and with the Boltzmann factor.

Where the states are sparsely taken, as in air at room temperature, the two forms are the same, and a gas of fermions behaves as a gas of bosons. Sparsely taken states are the *classical limit*, and the gases of Chapter 4 lie in the classical limit. Where the states are crowded, because the particles are many, light or cold, the forms differ entirely. Fermions fill the states one by one from the lowest up to a top, and at the lowest temperature every state below the top is full and every state above it empty. The full states are called the *Fermi sea*, and the energy of the top is the *Fermi level*. The electrons of a metal form such a sea (Chapter 6), and so do the electrons of a white dwarf star, whose sea holds the star up against its own weight (Chapter 13). Bosons gather many into the lowest state. As a gas of bosons is cooled at a fixed number, its chemical potential rises toward the lowest energy, and below a certain temperature a large share of all the particles crowd into the one lowest state together: *Bose-Einstein condensation*. It was first made in a thin gas in 1995, with atoms of rubidium-87, whose condensate first appeared "near a temperature of 170 nanokelvin" (Anderson, Ensher, Matthews, Wieman and Cornell, 1995), a nanokelvin being a billionth of a kelvin. Helium-4 shows its effects in the liquid as superfluidity, flow without friction (Chapter 9).

XIII. Light in a Box

Look through the spy hole of a hot kiln. Inside, the pots, the shelves and the walls all glow with one color, and the pots can hardly be told from the walls behind them, whatever they are made of. Heat a poker in a fire, and as it grows hotter it glows dull red, then orange, then yellow-white. The color of the glow tells the temperature, and it does not depend on what is glowing. What light does matter give out at a given temperature, and why does its color follow the temperature alone?

The inside of the kiln is light in balance with matter at one temperature. A body that takes in all the light that falls on it, reflecting none, is called a *black body*, and the light inside a closed cavity whose walls are at one temperature is the light a black body sends out at that temperature: *black-body radiation*. Photons are given off and taken in by the walls freely, so their number is not kept and their chemical potential is zero (Section XI), and any number of them can share a state, since the photon is a boson. So the photons in the cavity fill their states by the Bose-Einstein form of Box 2.5, with nothing fixing their number. In Box 2.6 I count the states and find the energy the light holds.

Box 2.6. The energy of light in a box goes as the fourth power of the temperature

Premises. (1) In a cavity of volume V, the number of states of one photon with momentum less than p is $2 \times (4\pi/3)p^3V/(2\pi\hbar)^3$: the states fill a ball in the three dimensions of momentum, as many for each unit of volume of momentum as Box 2.4, premise 1, gives, and each counts twice for the photon's two senses of turning (standard quantum mechanics). (2) A photon's energy is proportional to its momentum: $E = pc = h\nu$, with ν, read "nu", its frequency (standard physics). (3) The chemical potential of

the photons is zero, and each state holds on average $1/(e^{h\nu/kT} - 1)$ photons (Box 2.5, Section XI). (4) The integral of $x^3/(e^x - 1)$ from 0 to infinity is $\pi^4/15$ (mathematics).

Steps. By (1) and (2), the states with frequency between ν and $\nu + d\nu$, for each unit of volume, number $(8\pi\nu^2/c^3)\, d\nu$. By (3), each holds energy $h\nu/(e^{h\nu/kT} - 1)$, so the energy for each unit of volume and each unit of frequency is $u(\nu) = (8\pi h\nu^3/c^3)/(e^{h\nu/kT} - 1)$: Planck's law (Planck, 1901). Writing $x = h\nu/kT$ and using (4), the total energy for each unit of volume is $u = aT^4$, with $a = 8\pi^5k^4/(15h^3c^3) = 7.566 \times 10^{-16}$ joules for each cubic meter and each kelvin to the fourth power. The light leaving through a small hole in the cavity carries, for each square meter, σT^4, with $\sigma = ac/4 = 5.670374419 \times 10^{-8}$ watts for each square meter and each kelvin to the fourth power, the *Stefan-Boltzmann constant*. The peak of u, taken for each unit of wavelength, lies at the wavelength λ with $\lambda T = 2.897771955 \times 10^{-3}$ meter kelvin; taken for each unit of frequency, at $h\nu = 2.821\ kT$.

Result. The energy of light in balance at temperature T goes as T^4. The four is three plus one. Three powers come from the three dimensions of space: the number of states with energy below E grows as E^3, since it grows as the cube of the momentum and the momentum is proportional to the energy; one power comes from the energy each state holds, of order kT.

Josef Stefan found the fourth power in measurements (Stefan, 1879), and Boltzmann derived it from the pressure of light (Boltzmann, 1884). Planck found the whole spectrum, and in finding it he took the energy of the oscillators that send out and take in the light to come in quanta $h\nu$, the first step of the quantum theory. The peak moves with the temperature, as the poker shows: *Wien's law*, $\lambda T = 2.898 \times 10^{-3}$ meter kelvin (the value recommended in 2022 by the Committee on Data of the International Science Council, CODATA). It puts the peak of the Sun's light, at 5772 kelvin, near 502 nanometers, in the middle of what the eye sees, and the peak of a human body's glow, at about 310 kelvin, near 9.3 micrometers, far in the infrared, light of wavelengths longer than the eye can see (computed).

The largest black body there is fills the sky. *The Coming of the Kinds*, Chapter 13, follows the light that went free when the first atoms formed, about 370,000 years into our history, at 2,973 kelvin. The expansion has stretched its waves since, and it reaches us as the cosmic microwave background, at 2.72548 $\pm$ 0.00057 kelvin (Fixsen, 2009). Its spectrum is Planck's law at that temperature. The Far Infrared Absolute Spectrophotometer of the Cosmic Background Explorer satellite, which measured it from space, found that its departures from a black body are "less than 50 parts per million of the peak" (Fixsen, Cheng, Gales, Mather, Shafer and Wright, 1996). At that temperature the peak for each unit of frequency lies at 160.2 GHz, a gigahertz (GHz) being a thousand million waves in each second, and the peak for each unit of wavelength at 1.063 millimeters (the two differ because equal steps of frequency and of wavelength are not equal shares of the spectrum). The light holds 411 photons in each cubic centimeter (*The Coming of the Kinds*, Box 1.1) and 0.26 eV of energy in each cubic centimeter (computed, aT^4). Figure 2.2 draws the spectrum.

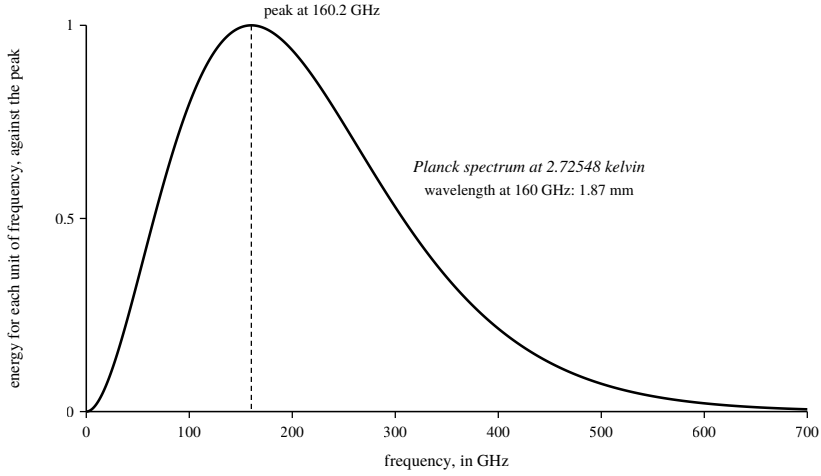


Figure 2.2. The spectrum of light in balance at 2.72548 kelvin, the temperature of the cosmic microwave background, drawn from Planck's law (Box 2.6): the energy for each unit of frequency, scaled so that the peak is 1, against the frequency in gigahertz. The peak lies at 160.2 GHz, and the energy falls to half the peak's at about 66 GHz and at about 307 GHz. The measured spectrum of the background lies on this curve to within fifty parts in a million of the peak.

XIV. Order Against Disorder

A pond freezes over on a winter night and thaws on a spring afternoon. In the ice the water molecules sit in a regular pattern, each bound to its neighbors, and in the water they tumble past one another. The same molecules choose order when it is cold and disorder when it is warm.

What decides the choice? Take a system in contact with a much larger one at temperature T, as the pond is with the air and the ground. The two together are found where their joint entropy is greatest (Section IV). When the system takes in an amount of energy E from its surroundings, the surroundings lose entropy E/T (Section VII). So the joint entropy is the system's own entropy S less E/T, and making that greatest is the same as making $E - TS$ least. A system held at a fixed temperature settles where its energy, less its temperature times its entropy, is least. That quantity is its *free energy*, $F = E - TS$, also called the Helmholtz free energy. At a given temperature it is the share of the system's energy that can be drawn off as work.

Ordered arrangements, bonded, aligned or packed, usually have less energy and less entropy than disordered ones. Their lower energy comes from what holds them. A bond lowers the energy: in Volume One, Chapter 11, I find that the bonding state of a shared pair of electrons holds two nuclei together at the separation of least energy. Alignment lowers the energy too: in Volume One, Chapter 9, I find that electrons whose spins point the same way keep apart, screen one another less and are held more strongly by the nucleus. Chapter 8 follows the same lowering when the

spins of many atoms line up in a magnet. Their lower entropy comes from what each kind of order fixes. A bond fixes electrons in shared states and atoms at set distances from one another. Alignment fixes directions that disorder leaves free to point anywhere. And every such fixing reduces the number of arrangements open to the system.

So the free energy weighs energy and entropy against each other. When the system is cold, T is small, the energy term E rules, and order wins, since order has the lower energy. When it is warm, the term TS rules, and disorder wins, since disorder has the larger entropy. Water freezes when cold and melts when warm because ice has less energy than water and less entropy.

Is ordered packing always the lower in entropy? It is usually, and two exceptions show where the rule comes from. Hard balls with no pull between them have only one energy, whatever their arrangement, so the free energy is decided by entropy alone. Yet when they are squeezed close enough they crystallize, as computer simulations found in 1957 (Alder and Wainwright, 1957; Wood and Jacobson, 1957). In a crowded jumble each ball is hemmed in by neighbors on every side, while in a regular packing at the same density each ball has more free room to rattle in its place. So above a certain density the crystal has more entropy than the disordered packing, and order wins by entropy. Balls filling 49.4 percent of the space or less stay disordered, and filling 54.5 percent or more they crystallize, with the two arrangements side by side in between (Hoover and Ree, 1968, as given by Pusey and others, 2009). The second exception is helium-3: below about 0.3 kelvin, solid helium-3 has more entropy than liquid helium-3. In the solid each atom sits in its own place, and the spin of its nucleus is free to point either way, two choices for each atom. The liquid is a crowd of fermions that fills its states one to a state up to a top (Box 2.5), a state being a state of motion with one direction of nuclear spin. So nearly every filled state of motion holds two atoms with opposite nuclear spins, and the spins have almost no free choices left. So squeezing the liquid where it meets the solid turns liquid into solid, the change takes in heat because the solid holds more entropy, and the helium cools: the ef-

fect predicted by Isaak Pomeranchuk (Pomeranchuk, 1950). So order has less entropy when it fixes positions or directions that disorder leaves free, and more when ordering frees room for a motion that crowding took away.

Melting and boiling are usually watched at a fixed pressure, not at a fixed volume. *Pressure* is the force for each unit of area with which a gas or a liquid presses on what holds it. The air at sea level presses with about 101,325 newtons on each square meter, a newton being the unit of force, and 101,325 newtons on a square meter is the standard atmosphere, a value fixed by definition. One newton on each square meter is a *pascal*, the unit of pressure, so the standard atmosphere is 101,325 pascals. A system held at a fixed temperature and a fixed pressure can also take room from its surroundings, and taking a volume V against the pressure P gives up PV of the surroundings' energy, so the surroundings lose entropy PV/T as well. The quantity that is least is then the *Gibbs free energy*,

$$G = E + PV - TS,$$

named for Josiah Willard Gibbs. Melting points and boiling points are found where the Gibbs free energies of solid and liquid, or of liquid and gas, for each molecule, are equal, and Chapter 3 uses the same quantity to say where a reaction settles.

XV. When a Change Happens at a Point

Drop ice into a glass of water and stir. The mixture cools to the melting point and stays there, the ice melting slowly and the water staying at one temperature, until the last of the ice is gone. The change between ice and water happens at one temperature. Why at one temperature, and not over a range?

For a system of many particles the change between order and disorder happens over a narrow range of temperature, narrower the more particles there are. The reason is the count. The free energy of each arrangement is a sum over its particles, so it is the number of particles N times a free en-

ergy for each particle. The weight of each arrangement goes as $e^{-F/kT}$ (Box 2.3, applied to the system as a whole in its surroundings), so the weight of one arrangement against the other is the exponential of N times the difference of their free energies for each particle, over kT. At the temperature where the two free energies for each particle are equal, the weights are equal. A small step to either side multiplies the difference by N in the exponent, the power to which e is raised in the weight, so the system goes over almost wholly to one arrangement within a step of temperature that shrinks as $1/N$. For 10^{24} molecules the range is far too narrow to find: the change happens at a point, one temperature for each pressure. Lars Onsager's exact solution of a model magnet in two dimensions, the first exact solution of a change of order in the limit of many particles, showed such a point emerging in the mathematics (Onsager, 1944).

The argument needs two distinct arrangements, whose free energies cross. So a true point appears in the limit of many particles only where something separates the two arrangements. A symmetry can separate them. In a magnet below its *Curie point* the spins of the atoms line up along one direction, which picks that direction out from all others, and above it they point every way and no direction is picked. A direction is either picked or not, with no arrangement between, so iron loses its magnetism at one temperature, 1043 kelvin, 770 degrees Celsius (Chapter 8). A jump can separate them. Ice and water differ by a definite amount of energy and entropy for each molecule, the heat that melting takes in, so they pass into each other only by that jump, and ice melts at one temperature. Liquid water and steam differ by such a jump too, but only below a definite temperature and pressure, the *critical point*, which for water is 647.096 kelvin and 22.064 million pascals (Wagner and Pruß, 2002). Above the critical point liquid and gas pass into each other smoothly as the temperature or the pressure changes, with no jump and no boiling at all, since nothing separates them there.

Where neither a symmetry nor a jump separates the arrangements, the change is a smooth *crossover*, however many particles there are. In *The Coming of the Kinds* I find two such changes in the early universe. In its Chapter 4 and Chapter 6, the Higgs field takes its value in a crossover, "a smooth change with no jump", centered at a temperature of 159.5 $\pm$ 1.5 GeV, written as an energy. In its Chapter 3 and Chapter 8, the binding of the quarks into protons, neutrons and other wholes is a crossover as well, near 156.5 $\pm$ 1.5 MeV. So the rule has its scope: a change between order and disorder is sharp, at one temperature, in the limit of many particles, where a symmetry or a jump separates the arrangements, and it is a smooth crossover where neither does.

At a fixed pressure, as I found in Section XIV, the arrangements trade places where their Gibbs free energies are equal, so a melting point or a boiling point is a point for each pressure. Water boils at a lower temperature high on a mountain than at the sea, where the air presses harder. Chapter 4 draws the whole map of the arrangements of water against temperature and pressure.

XVI. The Coldest State

A shelf of books in strict alphabetical order can be arranged in one way only. Let the order loosen, so that books by one author may stand in any order among themselves, and the arrangements multiply.

As a system is cooled, the Boltzmann factor of every state above the lowest falls toward zero. At the lowest temperature the system is in its ground state, the state of least energy it can have (Chapter 1, Section VI). Its entropy is then the logarithm of the number of its ground states, which is zero if there is only one. The rule for a system's entropy at the lowest temperature is the *third law of thermodynamics*, which Walther Nernst found from thermal measurements of chemical balances (Nernst, 1906).

In the form the counting gives it, as the temperature goes to its lowest value, the entropy of a system goes to the logarithm of the count of its ground states, zero for a single ground state.

A system cooled too fast to reach its ground state keeps an entropy above that value, its *residual entropy*, because the arrangements it was caught in stay as they were. Ice is the classic case. In ice each oxygen atom has four neighbors, and along the line to each neighbor lies one hydrogen atom, nearer one end or the other. Each oxygen must have exactly two hydrogens near it, to stay a water molecule. Linus Pauling counted the arrangements that keep that rule (Pauling, 1935). With two hydrogens for each oxygen, each free to sit near either end of its line, there are 2^{2N} placings for N molecules. Of the sixteen ways the four hydrogens round one oxygen can sit, six put exactly two near it, so the rule leaves a share 6/16 for each oxygen, and the count is $2^{2N} \times (6/16)^N = (3/2)^N$. The residual entropy is therefore $\ln(3/2)$ for each molecule, or $N_A k \ln(3/2) = 3.37$ joules for each kelvin and each mole. William Giauque and J. W. Stout measured 0.82 ± 0.05 calories for each degree and each mole, a calorie being 4.184 joules, so 3.4 ± 0.2 joules (Giauque and Stout, 1936). Glasses keep a residual entropy in the same way: a liquid cooled too fast to crystallize stiffens with its molecules caught in a disordered arrangement.

Why do such arrangements stay as they were? To pass from one arrangement to another, the particles must pass through arrangements of higher energy, and the share of the time they hold that much energy falls as the Boltzmann factor of the extra energy (Box 2.3). When the system is cold, that share is so small that the change is not made in any time that could be waited. The rates of such passages, over barriers of energy and through them, are the question of Chapter 3.

XVII. What the Counting Rests On

What does each result of this chapter rest on? I have built the results of this chapter in a definite order, and the order shows the answer.

Entropy, temperature and the zeroth law, the Boltzmann factor, the partition function and equipartition, the chemical potential and Saha's rule, the Fermi-Dirac and Bose-Einstein distributions, the light in a box, and the Boltzmann constant as a unit all follow by mathematics from three things: equal counting (Section II), the totals the system keeps, and exclusion. The second law adds one thing more, the traces the particles make of one another, which stay once they have reached many particles (Section V). Order against disorder adds that ordered arrangements usually have less energy and less entropy, which I argue in Section XIV from what bonding and alignment fix, together with the cases where ordered packing has more entropy and why. Rates of change among molecules add the two routes across a barrier of energy, over it or through it, which I argue in Chapter 3.

Everything rests on the first of these, equal counting. Equal counting comes from comparison: from the weight the motion keeps and the principle of identity (Section II). And the second law is the order in which the traces follow the acts that make them, counted over very many particles.

The results on which the counting rests are the standard results of the subject, found over the decades round 1900, and a reader can meet each of those results in the standard accounts under the names given here. Boltzmann's entropy is $S = k \ln W$ (Boltzmann, 1877). The second law states that the entropy of an isolated system does not decrease. Temperature is fixed by $1/T = dS/dE$, and equal temperature is balance, the zeroth law. A system in contact with a large one follows the Boltzmann factor $e^{-E/kT}$. Identical fermions follow the Fermi-Dirac distribution (Fermi, 1926) and bosons the Bose-Einstein distribution (Bose, 1924), both of which reduce to the Boltzmann factor where states are sparsely taken, and fermions fill a Fermi sea while bosons can gather into the lowest state. Systems in contact with a large one at fixed temperature make the free energy $F = E - TS$ least, and changes of order sharpen in the limit of many particles (Onsager, 1944). The third law gives zero entropy at the lowest temperature for a single ground state (Nernst, 1906). Black-body radiation

follows Planck's law (Planck, 1901), with total energy going as T^4 (Stefan, 1879; Boltzmann, 1884). Since 2019 the kelvin is defined by fixing the Boltzmann constant at exactly 1.380649×10^{-23} J/K, and k converts a temperature in kelvin to an energy.

In Use

Every engine that burns fuel works under Carnot's limit (Box 2.2). The limit, $1 - T_c/T_h$, depends on the temperatures alone. So a power station raises its steam as hot as its metals can bear and cools it as far as its river or its air allows, since every kelvin added to the hot side or taken from the cold side raises the share of heat that can become work. A real engine falls short of the limit, because the limit belongs to reversible change, and a real engine moves heat across differences of temperature, rubs, and lets gases rush. Each of those is a fast change, and each raises the entropy (Section VI), wasting part of the heat that a reversible engine would have turned to work.

A *refrigerator* runs the cycle backward: it uses work to carry heat out of a cold box and give it, with the work, to the warmer kitchen. The second law holds through it because the heat it gives out carries more entropy than the heat it takes in. A *heat pump* is the same machine set to warm a house: it takes heat from the colder air or ground outside and delivers it, with the work it uses, inside. Because it moves heat instead of making it, it delivers more heat than the work it uses. Box 2.2 bounds the gain at 14.7 for a room at 20 degrees Celsius warmed from air at 0 degrees. The heat must still flow across differences of temperature in the pump's coils, and in moderate climates heat pumps "can provide up to three times the energy they consume" (U.S. Department of Energy, Solar Decathlon, "Technology Spotlight: Heat Pumps").

A *thermal camera* sees the black-body glow of Section XIII. Every body sends out light by its temperature, and by Wien's law a body near 310 kelvin, a human body, glows most strongly near 9.3 micrometers, in the

infrared. Thermal cameras see the band from about 8 to 14 micrometers, where bodies near room temperature glow most and where the air lets infrared light through (LightPath Technologies, "What is Long Wave Infrared Technology?"). The glow grows as the fourth power of the temperature (Box 2.6), so a small difference of temperature makes a visible difference of brightness, and the camera shows a warm hand, a leaking window or an overheating wire against the cooler things around it, in the dark.

Summary

A many-body system keeps its total energy and has a vast number of microstates with that total, which no measurement of its totals tells apart and which its motion carries into one another while keeping their weight. The only weight among them is the one the motion keeps, which weighs them all alike, and a preference that no measurement registers is none, by the principle of identity. So every microstate with the system's totals counts alike: the postulate of equal a priori probabilities, which holds whether or not the motion passes through every microstate. Where an extra total is kept and can be registered, the count is made among the microstates with that total.

Entropy is the logarithm of the count of microstates, the measure that adds for independent systems. It counts the arrangements of the whole system, as distinct from the count of states of one particle. Almost all microstates lie near the macrostate of greatest entropy, and each macrostate of appreciably less entropy for each particle is outnumbered by a factor exponential in the number of particles. The band near the greatest entropy narrows as one over the square root of that number. Interacting particles leave traces in one another. In a system open to its surroundings the traces carried off are out of reach, so the entropy of the system with what left it never falls. In an isolated system a return would need traces gathered back from among alternatives that grow exponentially with the number of

particles, and it is found only where the traces have reached few particles, as in the spin echo. The rule that the entropy never falls is the second law, the direction of time that the count shows. Change slow enough for the system to stay in balance keeps the entropy, and faster change raises it.

Temperature is the energy it takes to raise the entropy by one unit. Equal temperatures exchange nothing on balance, heat flows from hotter to colder, and no engine turns more than $1 - T_c/T_h$ of its heat into work. No sorter that uses what it finds of the molecules gets round that limit, since clearing the memory that keeps its findings gives off at least kT ln 2 of heat for each bit. Temperature is measured in energy, and the Boltzmann constant, which fixes the kelvin, is a unit and not a fifth relation beside c, ħ, α and G. A small part of a large system takes each state with the Boltzmann factor $e^{-E/kT}$ (Box 2.3). From it come the partition function, equipartition, the speeds of molecules, the chemical potential and Saha's rule (Box 2.4). With exclusion, it gives the Fermi-Dirac and Bose-Einstein distributions (Box 2.5), which agree where states are sparse and differ where they are crowded, fermions filling a sea up to a top and bosons gathering into the lowest state. Light in a box follows the Bose-Einstein form with zero chemical potential, so its spectrum is Planck's and its energy goes as T^4, three powers from the dimensions of space and one from the photon's energy being proportional to its momentum (Box 2.6). The microwave background is that spectrum at 2.72548 kelvin.

A system at fixed temperature makes its free energy $E - TS$ least, and at fixed pressure its Gibbs free energy $E + PV - TS$. So order, which usually has less energy and less entropy, wins when cold and disorder when warm, and ordered packing can win by entropy where crowding is what disorder costs. The change is sharp, at one temperature, in the limit of many particles, where a symmetry or a jump separates the arrangements, and a smooth crossover where neither does. At the lowest temperature the entropy is the logarithm of the number of ground states, zero for one, and a system cooled too fast keeps a residual entropy.

The same counting says how often a molecule holds enough energy to change, and where a change among many molecules settles. With the counting in hand, how fast do molecules change, and where do they settle?

✶

KEY CONCEPTS

- **Many-body system.** Many particles taken together, with their total energy kept.
- **Microstate and macrostate.** One complete arrangement of a system, every particle's state given; and what is found of the system as a whole, its totals.
- **Equal a priori probabilities.** Every microstate with a system's totals counts alike; it follows from the weight the motion keeps and the principle of identity.
- **Principle of identity.** What no comparison can distinguish, in any way at all, even in principle, is one thing and not two (*The Quantum Passage*, Chapter 8, Section VI); a difference that no comparison can register is no difference (*Measurement*, Chapter 11, Section IV).
- **Ergodic hypothesis.** The statement that a system's motion passes through every microstate with its energy in time; equal counting holds with the closure that the kept energy gives, whether or not this holds.
- **Entropy.** The logarithm of the number of a system's microstates with its totals, $S = k \ln W$; it adds for independent systems.
- **Count of states.** The number of distinct ways one particle of a kind can be, apart from where it is and how it moves; a property of one particle, as distinct from the entropy of the whole.
- **Fluctuations.** The small changing departures of a system from its most probable macrostate; their relative size goes as one over the square root of the number of particles.

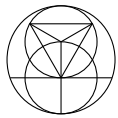
- **Decoherence.** The passing of the relations of phase among a particle's alternatives into its joint state with what it interacts with.
- **Second law of thermodynamics.** The entropy of an isolated system does not decrease; the traces the particles make of one another, which stay once they have reached many particles, counted.
- **Spin echo.** The return of the joint signal of nuclei drifted out of step, when a second pulse reverses the sense of every nucleus's drift; a return found because each trace was held in one nucleus.
- **Thermodynamic arrow of time.** The second law as a direction of time: the direction that the count shows.
- **Reversible and irreversible change.** A change slow enough that the system stays in balance at every step, which keeps the entropy; and a change too fast for that, which raises it.
- **Temperature.** The energy it takes to raise a system's entropy by one unit: $1/T = dS/dE$.
- **Zeroth law.** Two systems each in balance with a third are in balance with each other.
- **Heat; heat capacity.** Energy passed because of a difference of temperature; and the energy a system takes up for each rise of one unit in temperature, $C = dE/dT$.
- **Boltzmann constant; kelvin.** $k = 1.380649 \times 10^{-23}$ J/K, exact since 2019, a unit that converts a temperature in kelvin to an energy; the kelvin is the unit of temperature.
- **Work.** Energy passed by a force that moves something along its way; it carries no entropy.
- **Carnot's limit.** No engine working between T_h and T_c turns more than $1 - T_c/T_h$ of the heat it takes in into work.
- **Maxwell's sorter; memory; clearing a memory.** A device that lets the molecules of a gas pass by what it finds of their motion; a small system that keeps findings, one state for each finding, two states keeping one

bit; and the setting of a memory to one state whatever it held, which gives off at least kT ln 2 of heat for each bit (Landauer, 1961), so that no sorter lowers the entropy of everything together.

- **Refrigerator and heat pump.** An engine run backward, using work to carry heat from a colder body to a warmer one.
- **Boltzmann factor.** $e^{-E/kT}$, the weight with which a small part of a large system at temperature T takes a state of energy E.
- **Partition function.** Z, the sum of the Boltzmann factors of all a part's states, from which its averages follow.
- **Equipartition.** Each energy that goes as the square of a position or a velocity holds ½kT on average, when kT is large against its quanta.
- **Maxwell-Boltzmann distribution.** The range of speeds among the molecules of a gas: the Boltzmann factor of each speed's energy, times the v^2 ways of moving at that speed.
- **Chemical potential.** μ, the energy that adding one particle brings at fixed entropy and volume; particles pass from higher μ to lower; zero for photons.
- **Thermal wavelength.** The length of the wave of a particle moving at a gas's typical speed; a thin gas holds far fewer than one particle in each cube of that side.
- **Saha's rule.** $n_e n_p / n_H = (m_e kT/(2\pi\hbar^2))^{3/2} e^{-B/kT}$, the balance of free electrons and bound atoms (Box 2.4).
- **Fermion and boson.** A particle whose spin is an odd number of halves, of which no two of one kind share a state; and a particle whose spin is a whole number, of which any number can.
- **Fermi-Dirac and Bose-Einstein distributions.** $1/(e^{(\varepsilon - \mu)/kT} + 1)$ and $1/(e^{(\varepsilon - \mu)/kT} - 1)$, the average numbers of fermions and bosons in a state of energy ε (Box 2.5).
- **Classical limit.** States so sparsely taken that both distributions reduce to the Boltzmann factor.

- **Fermi sea; Fermi level.** The filled states of fermions at the lowest temperature, and the energy of the top of them.
- **Bose-Einstein condensation.** The gathering of a large share of a cold gas of bosons into its one lowest state.
- **Black body; black-body radiation.** A body that takes in all the light that falls on it; and the light in balance with matter at one temperature, which such a body sends out.
- **Planck's law; Stefan-Boltzmann constant; Wien's law.** The spectrum of black-body radiation; the constant $\sigma = 5.670374419 \times 10^{-8}$ W m^{-2} K^{-4} of the light it sends out, σT^4; and the peak wavelength, $\lambda T = 2.898 \times 10^{-3}$ m K.
- **Cosmic microwave background.** The light that went free when the first atoms formed, a black body today at 2.72548 kelvin.
- **Free energy.** $F = E - TS$, the quantity a system at fixed temperature makes least.
- **Pressure; pascal.** The force for each unit of area with which a gas or a liquid presses on what holds it; one newton on each square meter, the unit of pressure.
- **Mole; Avogadro constant.** A mole is $6.02214076 \times 10^{23}$ molecules, the Avogadro constant, exact by the definition of the mole.
- **Gibbs free energy.** $G = E + PV - TS$, the quantity a system at fixed temperature and pressure makes least.
- **Curie point; critical point.** The temperature at which a magnet loses its alignment, at a point because a symmetry separates the arrangements; and the temperature and pressure above which liquid and gas pass into each other with no jump.
- **Crossover.** A smooth change between arrangements with no jump and no point, where nothing separates them.
- **Third law of thermodynamics.** At the lowest temperature the entropy is the logarithm of the count of ground states, zero for one.

- **Residual entropy.** The entropy left in a system cooled too fast to reach its ground state; $\ln(3/2)$ for each molecule of ice.
- **Atomic mass unit.** A twelfth of the mass of an atom of carbon-12.



Chapter 3

Change Among Molecules

CHAPTER OVERVIEW

A reaction among molecules is a rearrangement of bonds, and nearly every rearrangement must pass through an arrangement of higher energy than where it starts, a barrier. There are two routes past a barrier. Over the top, the moving part, the few atoms whose motion carries the rearrangement, must hold the barrier's energy for a moment. The share of a gathering's microstates that place that much energy in the moving part falls as the exponential of the barrier over kT. So the rate of a reaction that goes this way follows the Arrhenius law, $e^{-E_a/kT}$ times a rate of attempts, and rises steeply with temperature (Box 3.1). The route over the barrier is the route of most chemistry at ordinary temperatures. On the route over the barrier the rate is set by how many ways the gathering of molecules holds its energy, which is why rates need the counting of ways of Chapter 2. Through the barrier, a light part can pass while holding less energy than the barrier, because its wave reaches past the region that confines it, a passing called tunneling. How likely that route is depends on the barrier's height and width and on the mover's mass, changes little with temperature, and rules when cold and for light movers. So hydrogen moves through its barrier in hours at 11 kelvin, and alpha decay, the sending out of a helium-4 nucleus by a heavy nucleus, goes wholly by tunneling. Where a reaction settles is a separate matter from how fast it goes. In balance, the chemical potentials of what goes in equal those of what comes out. So the amounts stand in a fixed ratio, the equilibrium

constant, set by the Gibbs free energy of the reaction: the law of mass action (Box 3.2), of which Saha's rule is the first example. A catalyst, a substance that opens a lower route over the barrier and is left unchanged, speeds the reaction both ways alike and leaves where it settles as it was. A heavier isotope, an atom of the same element with more neutrons, sits lower in its bond, so its barrier is effectively higher and it reacts more slowly. Deuterium, hydrogen with a neutron beside its proton, reacts up to about seven times more slowly than hydrogen at room temperature, and by more where tunneling plays a part. Oxidation and reduction are the passing of electrons from one atom to another. Set apart in two halves of an electrochemical cell, the passing drives a current, and the cell's voltage is the fall of the Gibbs free energy of the reaction for each charge passed (Box 3.3).

I. Fast and Slow

Chapter 2 ended with a question: with the counting in hand, how fast do molecules change, and where do they settle?

A box of matches can lie in a drawer for years, the wood and the head of each match beside the oxygen of the air, and nothing happens. Strike one, and in a second it is burning, giving out heat and light, and it burns until the wood is gone. The wood and the oxygen together hold more energy than the carbon dioxide and water they become, and that is why the burning gives out heat. Yet left to themselves, at the temperature of a drawer, they do not burn at all. Other reactions go at once. Drop a crystal of salt into water and it begins to dissolve as it touches, and mix an acid with a base and they react as fast as they can be stirred.

A *reaction* is a change in which molecules rearrange their bonds into other molecules: the atoms stay, and the pairs of electrons that join them (Volume One, Chapter 11) are shared in a new way. Its *rate* is how much

of it happens in each second. So the reader's question is this: why do some reactions go at once and others, even ones that would give out energy, not at all?

The answer needs the counting of Chapter 2. How fast bonds rearrange, and every property that depends on many particles moving at once, needs a counting of the ways a collection of particles can hold a given energy, and of how it shares that energy among its parts. A bond rearranges when, among all the ways the molecules share their energy, enough of it gathers in the few atoms that must move. How often that happens is a count, and I make that count.

II. Over the Barrier

Food keeps longer in a refrigerator than on a warm counter, and a cake bakes in an hour in a hot oven but would not bake in a year on a sunny windowsill. A few degrees, or a few tens of degrees, change the speed of a chemical change many times over. Why should so small a change of temperature make so large a change of speed?

Nearly every rearrangement of bonds must pass through an arrangement of higher energy than the one it starts from. To break one bond and make another, the atoms must be pulled partway out of the old arrangement before they settle into the new one, and partway, they are held by neither bond fully. That arrangement of highest energy along the way is the *barrier*, or the *transition state*, and the energy by which it lies above the starting arrangement is the reaction's *activation energy*, written E_a. The match is stable in the drawer because the barrier between wood and oxygen and their burning is high. The flame of the struck match supplies energy enough to carry the first molecules over it, and the energy each burning molecule gives out carries the next.

The first route past a barrier is over it. A rearrangement that must pass through an arrangement of higher energy can be reached by the moving part, the few atoms whose motion carries the rearrangement, holding the

barrier's energy for the moment. How often does the moving part hold that much? The moving part is a small part of a large system, the rest of the molecules and their surroundings, at temperature T, and Chapter 2, Box 2.3, gives the weight with which a small part holds a given energy: the Boltzmann factor. Box 3.1 counts the share of the ways that reach the top.

Box 3.1. The share of ways that reach the top

Premises. (1) A rearrangement goes from a starting arrangement, 1, to a final arrangement, 2, through a transition state whose energy lies E_a above arrangement 1. (2) The molecules are a small part of a large system at temperature T, so the probability that the moving part holds energy E is in proportion to the number of the part's states at E times $e^{-E/kT}$ (Chapter 2, Box 2.3). (3) For a motion along one direction, the share of the time in which that motion holds at least an energy E_a is $e^{-E_a/kT}$ (mathematics: the Boltzmann weights of the energies above E_a, summed, over those of all energies). (4) Each arrangement at the top passes on to arrangement 2 at a rate set by the motion across the top; and the number of ways of being at the top, against the number of ways of being in arrangement 1, is a ratio of counts of states that the shapes of the two arrangements fix.

Steps. By (2) and (3), the share of the molecules that hold, at a given moment, at least the energy E_a in the motion that leads over the barrier is $e^{-E_a/kT}$, times the ratio of the counts of states of (4). By (4), each such molecule crosses at a rate of attempts that changes slowly with temperature. So the rate of the reaction is $k_{rate} = A\, e^{-E_a/kT}$, with A, the prefactor, the rate of attempts times the ratio of the counts of states at the top and at the start. Taking the ratio of the rates at two temperatures removes A: $k_{rate}(T_2)/k_{rate}(T_1) = \exp[(E_a/k)(1/T_1 - 1/T_2)]$. For a reaction whose rate doubles between 298.15 kelvin (25 degrees Celsius) and 308.15 kelvin, this gives $E_a = k \ln 2/(1/298.15 - 1/308.15) = 0.549$ eV for each molecule, 52.9 kilojoules for each mole. At 298.15 kelvin the share of the molecules that hold that much is $e^{-21.36}$, 5.3×10^{-10}.

Result. The rate of a reaction that goes over its barrier is A $e^{-E_a/kT}$: the Arrhenius law (Arrhenius, 1889). The factor $e^{-E_a/kT}$ is the share of the ways of holding the system's energy that place at least E_a in the moving part, and the prefactor A counts how many ways there are of being at the top against how many of being at the start. An activation energy of 0.549 eV doubles the rate for each rise of ten degrees near room temperature, though only about one molecule in two billion holds that much at any moment.

The Arrhenius law is named for Svante Arrhenius, who found it from measured rates and wrote of the reaction he studied that "at ordinary temperatures, the rate increases by 10 to 15 per cent for each one-degree rise in temperature" (Arrhenius, 1889). Henry Eyring later counted the states at the top of the barrier and gave the prefactor its form, the theory of the transition state (Eyring, 1935). The rate rises steeply with temperature for this route, because the share $e^{-E_a/kT}$ is small and changes fast: a rise of ten degrees near room temperature changes kT by only three percent, yet it doubles the rate when E_a is twenty times kT. Because the share of molecules with energy enough to cross the barrier is small and changes fast, the match waits and the food keeps. At ordinary temperatures the share of molecules with energy enough to cross a high barrier is too small for the reaction to be seen, and heating a little of the matter, as the struck match does, raises that share by many powers of ten.

The rate of the route over the barrier needs the counting of ways of Chapter 2. A bond rearranges among many particles that share their energy, and the rate of the route over the top is set by how many ways the gathering of molecules can hold its energy at the start and at the top. Both parts of the rate are such counts: the share $e^{-E_a/kT}$, and the ratio of counts in the prefactor. At ordinary temperatures most rearrangements of bonds go over the barrier, by this route, so most rates of chemistry are

counts of ways. The rate at which a single particle passes through a barrier is another matter, set by the particle's wave alone, as the next section shows.

III. Through the Barrier

Shout at a closed door, and a listener on the other side hears you, faintly. A ball thrown at the door bounces back, every time. The sound, a wave, gets partly through. Can a reaction go when no molecule holds the energy to climb its barrier?

The second route past a barrier is through it. A rearrangement that must pass through an arrangement of higher energy can also be reached by the moving part passing through the barrier while holding less energy than the barrier, because the part's wave extends past the region in which the part is confined. The passing of a part through a barrier while the part holds less energy than the barrier is *tunneling*. Volume One, Chapter 7, found that a bound electron is found as a wave, and the same holds for an atom or a nucleus. Inside a region where its energy is less than the barrier, its wave falls away gradually from the edge, and if the barrier is thin enough a small part of the wave reaches the far side. That small part gives the chance of passing through.

How likely this route is, the chance of passing through, is set by the barrier and by the mover, and hardly at all by the temperature. Take a barrier of width d whose top lies an energy V above the mover's energy, with m the mover's mass. The share of the wave that gets through falls as $\exp(-2d\sqrt{(2mV)}/\hbar)$ (standard quantum mechanics, in the approximation for a barrier much higher than the mover's energy of motion within it). Three things make tunneling likely: a thin barrier, a low one, and a light mover. The mass enters under the square root, so a mover with twice the mass has an exponent (the power to which e is raised) larger by $\sqrt{2}$. Deuterium, the form of hydrogen whose nucleus holds a neutron beside its proton, has twice hydrogen's mass, so in place of hydrogen it has an ex-

ponent larger by $\sqrt{2}$. And a mover 1836 times heavier than an electron, a proton, has an exponent 43 times the electron's for the same barrier. The chance of tunneling changes little with temperature, since warming changes the barrier and the mover's energy only a little.

So the two routes trade places with temperature and with mass. When warm, the route over the top rules for most reactions, because the share $e^{-E_a/kT}$ is large enough. When cold, that share falls toward nothing, while the chance of tunneling stays, and tunneling rules. Light movers tunnel most. Electrons pass readily between molecules by tunneling, and through proteins, the large molecules that do the work of living cells, as well (Beratan, Betts and Onuchic, 1991), and among atoms hydrogen is the one that tunnels most in chemistry. Peter Schreiner and his colleagues made hydroxymethylene, a molecule of one carbon, one oxygen and two hydrogens that holds far more energy than the formaldehyde it can become. They trapped it in frozen argon at 11 kelvin, far too cold to cross its barrier by the route over the top. It "rearranges with a half-life of just 2 hours" to formaldehyde, by a hydrogen atom tunneling from the oxygen to the carbon (Schreiner et al., 2008), a half-life being the time in which half of a sample has changed. At the far end of the scale of energies, alpha decay, in which a heavy nucleus sends out a helium-4 nucleus, goes wholly by tunneling. The helium nucleus holds too little energy to climb over the barrier of the electric push, and it passes through it (Gamow, 1928; Volume One, Chapter 5, follows the decay and its rates).

The conclusion of Section II, that rates rise steeply with temperature, therefore holds for the route over the top, which is most chemistry at ordinary temperatures. The route through the barrier gives rates that change little with temperature, and it is the reason that some reactions still go at a few kelvin, as the hydroxymethylene in frozen argon does, where the route over the top is closed.

IV. Where a Reaction Settles

A busy bridge joins two towns. All day people cross it both ways, and if more cross one way than the other, the town they leave thins and the town they reach fills, until as many cross each way in every hour. The crossing never stops, but the numbers in the two towns stay where they settled. Where does a reaction that runs both ways settle?

A reaction that can run both ways settles in the same manner. Molecules of what goes in become molecules of what comes out, and molecules of what comes out turn back, each at its own rate. The amounts change until the two rates are equal, and then they stay. That settled state is the reaction's *chemical equilibrium*, the balance of Chapter 2 for a reaction. How fast the reaction gets there is the question of Sections II and III, and where it settles is a separate question, which the counting answers.

In balance, the chemical potentials of what goes in add up to those of what comes out (Chapter 2, Section XI). For a thin gas or a dilute solution, the chemical potential of each kind of molecule grows with the logarithm of its concentration, its number in each unit of volume (Chapter 2, Box 2.4, where the number for each unit of volume goes as $e^{\mu/kT}$). So the balance of chemical potentials fixes a ratio of concentrations. Box 3.2 carries the derivation.

Box 3.2. The law of mass action from the counting

Premises. (1) A reaction $a\,A + b\,B \leftrightarrow c\,C + d\,D$, in which a molecules of A and b of B become c of C and d of D (the letters here naming kinds of molecule, apart from the prefactor A of Box 3.1), is in balance when $a\mu_A + b\mu_B = c\mu_C + d\mu_D$ (Chapter 2, Section XI). (2) In a thin gas or a dilute solution, the chemical potential of a kind X at concentration [X] is $\mu_X = \mu_X^\circ + kT \ln([X]/c^\circ)$, where μ_X° is its value at a standard concentration c° (Chapter 2, Box 2.4: the number for each unit of volume goes as $e^{\mu/kT}$). (3) The Gibbs free energy of the reaction, for each set of molecules that re-

act, at the standard concentrations, is $\Delta G^\circ = c\mu_C^\circ + d\mu_D^\circ - a\mu_A^\circ - b\mu_B^\circ$ (standard thermodynamics: the chemical potential of a kind is the change in the Gibbs free energy of Chapter 2, Section XIV, when one molecule of that kind is added at fixed temperature and pressure; this is the same quantity as the energy that one more molecule brings at fixed entropy and volume, the form of Chapter 2, Section XI, since each is the change, on adding one molecule, of the energy that fits the quantities held fixed).

Steps. Put (2) into (1) and gather the logarithms: $kT \ln\{([C]/c^\circ)^c([D]/c^\circ)^d/[([A]/c^\circ)^a([B]/c^\circ)^b]\} = -\Delta G^\circ$. So the ratio $K = ([C]/c^\circ)^c([D]/c^\circ)^d/[([A]/c^\circ)^a([B]/c^\circ)^b]$ equals $e^{-\Delta G^\circ/kT}$ in balance. For a mole of reactions in place of one, ΔG° is multiplied by the Avogadro constant N_A, and kT by N_A, which turns k into the gas constant $R = N_A k = 8.314$ joules for each kelvin and each mole: $K = e^{-\Delta G^\circ/RT}$. In balance the forward and backward rates are equal. Each rate goes as the product of the concentrations of what it starts from, times a factor that depends on the temperature but not on the concentrations, the reaction's rate constant, so K is also the ratio of the forward rate constant to the backward one.

Result. In balance, the concentrations of what comes out, over those of what goes in, each raised to the power of its number in the reaction, stand in a fixed ratio K, the *equilibrium constant*, set by the Gibbs free energy of the reaction and the temperature: $K = e^{-\Delta G^\circ/RT}$. The fixed ratio K of the concentrations in balance is the *law of mass action*.

Saha's rule (Chapter 2, Box 2.4) is the law's first example: the reaction of an electron and a proton into a hydrogen atom. There the binding energy stands in the place of ΔG°, and the room a free electron has stands in the place of the standard concentration. A reaction whose ΔG° is negative by many times RT settles almost wholly on the side of what comes out. One whose ΔG° is positive by many times RT settles almost wholly on the side of what goes in. And one whose ΔG° is near zero settles with both present.

Where a reaction settles and how fast it gets there are different things, and a diamond shows the difference. At room temperature and the pressure of the air, graphite, the soft black form of carbon in a pencil, has the lower Gibbs free energy. Turning a mole of diamond into graphite lowers it by 2.900 kilojoules (*Lange's Handbook of Chemistry*, Dean, 1999), so in balance carbon would be graphite. Yet a diamond lasts for longer than anyone has watched one, because the barrier between the two arrangements of carbon atoms is so high that at room temperature the route over the top is closed. The equilibrium constant says where the carbon would settle, and the barrier says that it stays a diamond for longer than any time that matters.

V. Catalysts

Two valleys are divided by a high mountain range, and the only road between them climbs over a high pass. Find a lower pass through the same range and build a road over it, and travelers cross in both directions far more easily, though they still climb. The valleys themselves stay where they were. Can a reaction be made faster without heating it?

A *catalyst* is a substance that opens a new route for a reaction, with a lower barrier, and is left unchanged at the end. A surface of metal, on which molecules settle and their bonds loosen, is one kind. An *enzyme*, a large molecule of a living cell shaped to hold the reacting molecules in the arrangement of the transition state, is another. Lowering the barrier by an amount ΔE multiplies the rate over the top by $e^{\Delta E/kT}$, so even a modest lowering speeds a reaction enormously. An enzyme of living cells, orotidine 5′-monophosphate decarboxylase, does its reaction with a half-life of 18 milliseconds (Miller, Hassell, Wolfenden, Milburn and Short, 2000). The same reaction in water at room temperature, with no enzyme, has a half-life of 78 million years (Radzicka and Wolfenden, 1995), so the enzyme speeds it by about 10^{17} (computed from the two half-lives).

A catalyst brings a reaction to the same balance it would reach without it. The route it opens is a route between the same two arrangements, and the reaction running backward passes through the same transition state as the reaction running forward. So the catalyst lowers the barrier by the same amount in both directions and multiplies both rates by the same factor. The equilibrium constant is the ratio of the forward and backward rates (Box 3.2), so the equilibrium constant stays as it was: a catalyst brings a reaction to balance sooner, at the same balance. It speeds only the reactions that the Gibbs free energy allows, as a lower pass speeds travel between the valleys and makes no water run uphill.

VI. Heavier Atoms React More Slowly

Hang a light ball and a heavy one from two springs of the same stiffness, and set both bouncing. The heavy one bounces more slowly. Does the mass of an atom change how fast its bonds react, when the strength of a bond does not depend on that mass?

A bond between two atoms is such a spring. An atom of deuterium, with a proton and a neutron in its nucleus, has twice the mass of an atom of hydrogen while making the same bonds, since the electrons that make the bond see the same charge. So a bond to deuterium vibrates more slowly than the same bond to hydrogen. A vibrating bond, like every bound system, has a ground state, the state of least energy it can have. Its energy there is half a quantum of its vibration, hf/2, with f its frequency, and this least energy is the *zero-point energy* (standard quantum mechanics; Volume One, Chapter 7, found that confinement always costs energy). The slower bond to deuterium therefore sits lower in its well, the hollow of energy in which the bond holds its atoms, than the bond to hydrogen.

When the reaction breaks that bond, the vibration along it is lost at the transition state, and with it the zero-point energy that the bond held. So the barrier, measured from where the bond starts, is higher for deuterium by the difference of the two zero-point energies. A vibration's frequency is

written, in the measurement of the infrared light the bond takes in, as the number of waves of that light in each centimeter, and the frequency is in proportion to it. A bond of carbon to hydrogen vibrates at about 2,900 waves for each centimeter, and the same bond to deuterium at about 2,100 (standard infrared spectroscopy). The frequency goes as one over the square root of the reduced mass of the pair, which Chapter 1, Section VI, defines, so the two zero-point energies differ by 0.0479 eV (computed). Over the barrier, the rate for hydrogen against deuterium is then $e^{0.0479/0.0257}$, about 6.4, at room temperature, 298 kelvin, where kT is 0.0257 eV (Box 3.1 with that change of barrier). The largest ratios found for reactions going over the top are about seven at room temperature (Westheimer, 1961). This slowing of a reaction when a heavier isotope takes the place of a lighter one is the *kinetic isotope effect*. Where tunneling carries part of the reaction, the ratio is larger, because the exponent of tunneling grows with the square root of the mass (Section III), and doubling the mass cuts the share that tunnels by far more than it raises the barrier.

So heavier isotopes react more slowly, and the size of the slowing tells which route a reaction takes and which bond it breaks. Chapter 12 follows the isotope effects of chemistry and their uses, among them medicines in which deuterium takes the place of hydrogen so that the body breaks them down more slowly.

VII. Electrons Passing Between Atoms

Leave an iron nail out in the rain, and in a few weeks it is coated in red-brown rust. Burn a candle, and the wax and the oxygen of the air become carbon dioxide and water. The two changes look nothing alike, one slow and cold, the other fast and hot. What do they share?

Both are the passing of electrons from one kind of atom to another. Volume One, Chapter 11, found the far end of this passing in the bond of salt. An atom of sodium gives up its outer electron, at a cost of 5.14 eV, and an atom of chlorine takes it in, gaining 3.61 eV. The pull between the

two charged atoms, gathered over the whole crystal, more than pays the difference. Between those two ends, the shared pair of a bond and the electron wholly passed over, lie the bonds in which one atom pulls the shared pair closer than the other does.

Chemists keep account of the passing with a count. The *oxidation state* of an atom in a molecule is the charge it would carry if the shared electrons of each of its bonds were given wholly to the atom of the pair that pulls them harder. In water, each hydrogen is counted $+1$ and the oxygen -2, and in the oxygen of the air, O_2, where the two atoms pull alike, each is 0. *Oxidation* is the loss of electrons, a rise of an atom's oxidation state, and *reduction* is the gain of electrons, a fall. Every electron lost by one atom is gained by another, so oxidation and reduction always go together, and a reaction that passes electrons is called a reaction of oxidation and reduction.

In rust, iron goes from 0 to $+3$ and is oxidized, and the oxygen goes from 0 to -2 and is reduced. In a burning candle or a gas flame, the carbon goes from -4 in methane, the gas of a kitchen burner, to $+4$ in carbon dioxide, and the oxygen again from 0 to -2. Oxygen is the strongest taker of electrons among the common elements after fluorine: on the scale of Linus Pauling, as Allred revised it, fluorine stands at 3.98 and oxygen next at 3.44 (Volume One, Chapter 11, Section IX). The account by oxidation states applies to any atom that gives up electrons to any other, whether or not oxygen takes part. Both reactions have a large fall of Gibbs free energy, and both have a barrier. Iron in dry air rusts hardly at all, and wet iron rusts readily, because water carries the passing of electrons along at the iron's surface by another route (standard accounts of the corrosion of iron). And a gas burner must be lit because the barrier of methane and oxygen is high.

VIII. The Electrochemical Cell

Set a strip of zinc in a cup of zinc salt dissolved in water, and a strip of copper in a cup of copper salt dissolved in water. Join the two cups with a strip of paper soaked in salt water, and join the two metal strips with a wire through a small lamp. The lamp lights. Where does the lamp's energy come from, and what sets the voltage that drives it?

In that cell the zinc gives up electrons and passes into the water as zinc ions, and the copper ions in the other cup take electrons in and settle on the copper strip as metal. Written in symbols, $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$, where Cu^{2+} is a copper atom that has lost two electrons and Zn^{2+} a zinc atom that has lost two. Dropped into one beaker together, the zinc and the copper ions would make the same exchange directly, and the energy would come out as heat. In the cell the two halves of the reaction are set apart, so the electrons travel from the zinc to the copper ions only through the wire, and on the way they do work in the lamp. The salt-soaked paper lets ions move between the cups to keep each cup without a net charge. The two cups, joined by the wire and by the salt-soaked paper, are an *electrochemical cell*. An electrochemical cell is a reaction of oxidation and reduction with the reaction's two halves set apart, so that the electrons the reaction passes run through an outer circuit as a *current*, charge in motion. The metal strips are its *electrodes*. The one where oxidation happens, the zinc, is the *anode*, and the one where reduction happens, the copper, is the *cathode*. John Frederic Daniell described a cell of this kind, zinc against copper (Daniell, 1836).

The cell's voltage measures the Gibbs free energy of its reaction, a voltage between two points being the energy that each unit of charge gains or gives up in passing from one to the other. Chapter 2, Section XIV, found that at a fixed temperature and pressure a system settles where its Gibbs free energy is least. It found too that at a fixed temperature the free energy F is the share of a system's energy that can be drawn off as work.

At a fixed temperature and a fixed pressure the same reasoning holds, with the room PV that the system takes from its surroundings counted in. It makes the fall of the Gibbs free energy the most work that a change can give, other than the work of pushing back the surroundings (standard thermodynamics). Box 3.3 turns that work into a voltage.

Box 3.3. The voltage of a cell from the Gibbs free energy

Premises. (1) Each reaction in the cell passes n electrons through the outer circuit; for zinc and copper ions, $n = 2$. (2) At fixed temperature and pressure, the most work a reaction can give, other than the work of pushing back the surroundings, is the fall of its Gibbs free energy, $-\Delta G$, and a cell run slowly, reversibly, gives that much (standard thermodynamics, with the Gibbs free energy of Chapter 2, Section XIV, and the reversible change of Chapter 2, Section VI). (3) A charge q passing through a voltage E_{cell} does work qE_{cell} (standard electromagnetism); the letter E_{cell} names the cell's voltage, apart from the energies E of Chapter 2. (4) The charge of a mole of electrons is the *Faraday constant*, $F = N_A e = 96{,}485.33$ coulombs for each mole, the coulomb being the unit of charge, with $e = 1.602176634 \times 10^{-19}$ coulomb and N_A, both exact by the definitions of the international system of units. (5) Each half of a cell has a *standard electrode potential*, its voltage against a hydrogen electrode, a half cell of hydrogen gas bubbled over platinum in acid, taken as zero, with every concentration at its standard value: -0.7618 volt for zinc ions becoming zinc and $+0.3419$ volt for copper ions becoming copper (*CRC Handbook of Chemistry and Physics*, 84th edition, 2004, CRC being the name of its publisher). (6) The law of mass action (Box 3.2) and its form $\Delta G = \Delta G^\circ + RT \ln Q$, where Q is the ratio of concentrations of Box 3.2 at the concentrations the cell actually has (Chapter 2, Box 2.4; Box 3.2, premise 2).

Steps. By (1), (3) and (4), a mole of reactions run reversibly passes charge nF through the voltage E_{cell}, doing work nFE_{cell}; by (2), $nFE_{cell} = -\Delta G$, so $E_{cell} = -\Delta G/(nF)$. By (5), the zinc and copper cell at standard concentrations has $E_{cell}^\circ = 0.3419 - (-0.7618) = 1.104$ volts, so $\Delta G^\circ = -2 \times 96{,}485 \times 1.104$ joules $= -213$ kilojoules for each mole. By (6), $E_{cell} = E_{cell}^\circ$

$- (RT/(nF))$ ln Q, the *Nernst equation*; at 298.15 kelvin $RT/F = 0.02569$ volt, so a tenfold change of Q changes E_{cell} by $0.0592/n$ volt. For hydrogen and oxygen making liquid water, $\Delta G° = -237.14$ kilojoules for each mole (*Lange's Handbook of Chemistry*, Dean, 1999), with $n = 2$, so $E_{cell}° = 237{,}140/(2 \times 96{,}485) = 1.229$ volts, the value the same tables give for the oxygen electrode against hydrogen.

Result. A cell's voltage is the fall of the Gibbs free energy of its reaction for each charge passed: $E_{cell} = -\Delta G/(nF)$. The zinc and copper cell gives 1.10 volts; a cell of hydrogen and oxygen gives 1.23 volts; and the voltage falls, as the Nernst equation says, as the cell's reaction approaches balance, reaching zero when it is there.

So a battery is a reaction kept from reaching balance until a circuit is closed. Its voltage is set by which two half reactions it pairs, through the Gibbs free energy, and the amount of charge it can give is set by how much of its reacting matter it holds. A cell can also be run backward: a voltage larger than its own, applied from outside, drives its reaction the other way, and that is how a rechargeable battery is charged. It is also how the metals that give up electrons most readily are won from their ores. Aluminum is won by passing a current through alumina, its oxide, dissolved in a bath of molten fluorides, as Charles Martin Hall patented in 1889 ("dissolving alumina in a fused bath ... and then passing an electric current through the fused mass", Hall, 1889). Sodium "is now obtained commercially by the electrolysis of absolutely dry fused sodium chloride", electrolysis being exactly this driving of a reaction by a current (Los Alamos National Laboratory, Periodic Table of Elements, "Sodium").

In Use

Every flame is the route over the barrier kept going by its own heat. Burning a mole of methane, the gas of a kitchen burner, with oxygen into carbon dioxide and liquid water gives out 890 kilojoules, 9.2 eV for each mo-

lecule (National Institute of Standards and Technology, Chemistry WebBook, as collected by Cheméo), far more than the barrier. Once a spark lifts the first molecules over the barrier, the energy they give out heats their neighbors. The share of neighbors holding enough energy to cross then rises by the Boltzmann factor, and the flame runs through the mixture as fast as the gas can feed it. Engines and furnaces are built on that rise, and on Carnot's limit (Chapter 2, Box 2.2), which sets how much of the heat can become work.

Batteries and fuel cells take the same reactions of oxidation and reduction and set their halves apart (Section VIII). A lithium-ion cell, of the kind in a telephone or an electric car, has a nominal voltage of 3.6 or 3.7 volts (EL-CELL, "What is the nominal voltage of a lithium-ion battery?"). The voltage is large because lithium gives up its electron so readily: its standard electrode potential is −3.0401 volts (*CRC Handbook of Chemistry and Physics*, 84th edition), the most negative of the table. Charging drives its reaction backward with a voltage from outside. A *fuel cell* is a cell fed its reacting matter continuously. Hydrogen gives up electrons at one electrode and oxygen takes them in at the other, making water, with at most the 1.23 volts of Box 3.3. So the energy of burning hydrogen comes out as a current instead of a flame. Carnot's limit belongs to heat engines, and a fuel cell, which runs on no flow of heat, is bounded by the fall of the Gibbs free energy instead.

The catalytic converter of a car uses catalysts to clean its exhaust. Its ceramic honeycomb is lined with platinum, palladium and rhodium (International Union of Pure and Applied Chemistry, teaching material on the catalytic converter). On the surfaces of those metals, three reactions go at the temperature of the exhaust that would hardly go at all in the gas alone (the same source). Carbon monoxide is oxidized to carbon dioxide, unburned fuel to carbon dioxide and water, and the oxides of nitrogen are reduced to nitrogen. The metals lower the barriers, and where the reactions settle is set by their Gibbs free energies alone (Section V). The three reactions settle far on the side of the cleaner gases. For carbon monoxide burning to carbon dioxide, K is about 10^{45} at room temperature and still

about 10^{14} at 800 kelvin. For carbon monoxide and nitric oxide turning into carbon dioxide and nitrogen, K is about 10^{120} at room temperature and 10^{38} at 800 kelvin. Both are computed by Box 3.2 from the measured heats and entropies of the gases, as the NIST Chemistry WebBook gives them from Chase (1998).

The Haber process, which makes ammonia from the nitrogen of the air and hydrogen, uses every result of this chapter at once. The reaction $N_2 + 3H_2 \leftrightarrow 2NH_3$ has $\Delta G^\circ = -32.8$ kilojoules at room temperature (twice the -16.4 kilojoules of each mole of ammonia, *Lange's Handbook of Chemistry*, Dean, 1999). So by the law of mass action ammonia is strongly favored there, with $K = 5.6 \times 10^5$ (computed, Box 3.2). Yet at room temperature nothing happens, because the triple bond of the nitrogen molecule makes the barrier enormous. So the process runs hot, at 400 to 500 degrees Celsius, for the rate (Appl, 1997). It runs over a promoted iron catalyst, iron with small amounts of other substances, its promoters, added to make it work better, to lower the barrier (the same source). And it runs at pressures above 100 bar, a bar being 100,000 pascals, about the pressure of the air (the same source). The heat that gives the rate pushes the balance back toward nitrogen and hydrogen. The reaction gives out 91.8 kilojoules for each two moles of ammonia made (computed from the measured heats of forming the gases, NIST Chemistry WebBook, from Chase, 1998). Since $G = E + PV - TS$ (Chapter 2, Section XIV), ΔG° is the heat taken in at fixed pressure less T times the change of entropy, and in $\Delta G^\circ/RT$ the heat is divided by the temperature. So the heat given out favors ammonia less and less as the temperature rises. K falls to about 3×10^{-4} at 700 kelvin, 427 degrees Celsius (computed, Box 3.2, from the same measured heats and entropies). The pressure pushes the balance toward ammonia. Raising the pressure tenfold raises every concentration tenfold. In the ratio of Box 3.2 two molecules of ammonia stand above and four molecules of nitrogen and hydrogen below, so the ratio falls a hundredfold below K, and the reaction runs on toward ammonia until the ratio climbs back to K. Fertilizer

made from that ammonia fed an estimated 48 percent of the world's people in 2008 (Erisman, Sutton, Galloway, Klimont and Winiwarter, 2008).

Summary

A reaction is a rearrangement of bonds, and nearly every rearrangement passes through a transition state of higher energy, its barrier. There are two routes past a barrier. Over the top, the moving part must hold the barrier's energy for a moment. The share of the ways of holding the system's energy that place that much in the moving part is $e^{-E_a/kT}$. So the rate is A $e^{-E_a/kT}$, the Arrhenius law, with the prefactor counting the ways at the top against those at the start (Box 3.1). That route rules for most chemistry at ordinary temperatures, and its rate rises steeply with temperature. It is why rates need the counting of ways: the rate at which many molecules rearrange is set by how many ways they hold their energy among them. Through the barrier, a part can pass while holding less energy than the barrier, because its wave reaches past the region that confines it. The chance of passing that way is set by the barrier's height and width and the mover's mass, and it changes little with temperature. It rules when cold and for light movers, as in hydrogen tunneling at 11 kelvin and in alpha decay.

Where a reaction settles is separate from how fast it goes. In balance the chemical potentials of what goes in equal those of what comes out. So the concentrations stand in the ratio $K = e^{-\Delta G^\circ/RT}$, the law of mass action, of which Saha's rule is the first example (Box 3.2). K is also the ratio of the forward and backward rate constants. A catalyst opens a lower route over the barrier, speeds both directions by one factor, and leaves K unchanged. A heavier isotope sits lower in its bond by the difference of zero-point energies, so it reacts more slowly. Over the top, at room temperature, deuterium reacts up to about seven times more slowly than hydrogen, and by more where tunneling plays a part. Oxidation and reduc-

tion are the loss and gain of electrons, kept in account by oxidation states. Set apart in an electrochemical cell, they drive a current. The cell's voltage is the fall of the Gibbs free energy for each charge passed, $E_{cell} = -\Delta G/(nF)$, and it falls to zero by the Nernst equation as the reaction reaches balance (Box 3.3).

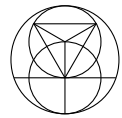
So far the molecules have been taken one reaction at a time. Molecules gather into gases, liquids and stranger things. What are those?

✶

KEY CONCEPTS

- **Reaction; rate.** A change in which molecules rearrange their bonds into other molecules; and how much of it happens in each second.
- **Barrier; transition state; activation energy.** The arrangement of highest energy that a rearrangement passes through, and the energy E_a by which it lies above the start.
- **Arrhenius law.** The rate of a reaction over its barrier, $A\, e^{-E_a/kT}$: the share of the ways that place E_a in the moving part, times a prefactor of attempts and of counts of states (Box 3.1).
- **Tunneling.** The passing of a part through a barrier while holding less energy than the barrier, because its wave reaches past the region that confines it; its chance falls as $\exp(-2d\sqrt{(2mV)}/\hbar)$.
- **Chemical equilibrium.** The settled state of a reaction, in which it runs as fast forward as backward.
- **Equilibrium constant; law of mass action.** $K = e^{-\Delta G^\circ/RT}$, the fixed ratio, in balance, of the concentrations of what comes out to those of what goes in, each raised to its number in the reaction (Box 3.2).
- **Gas constant.** $R = N_A k = 8.314$ joules for each kelvin and each mole, the Boltzmann constant for a mole.
- **Catalyst; enzyme.** A substance that opens a route of lower barrier and is left unchanged, speeding a reaction both ways alike; an enzyme is a catalyst made by a living cell.

- **Isotope; deuterium.** An atom of the same element with a different number of neutrons; deuterium is hydrogen whose nucleus holds a neutron beside its proton.
- **Half-life.** The time in which half of a sample has changed.
- **Zero-point energy.** The energy a vibrating bond keeps in its ground state, half a quantum of its vibration.
- **Kinetic isotope effect.** The slower reaction of a heavier isotope, from its lower zero-point energy and, where tunneling plays a part, from its smaller tunneling.
- **Oxidation state.** The charge an atom would carry if the shared electrons of each of its bonds were given wholly to the atom of the pair that pulls them harder.
- **Oxidation and reduction.** The loss and the gain of electrons, a rise and a fall of oxidation state, always together.
- **Electrochemical cell; electrode; anode; cathode.** A reaction of oxidation and reduction with its halves set apart, so that its electrons run through an outer circuit; its metal strips, oxidation at the anode and reduction at the cathode.
- **Faraday constant.** $F = N_A e = 96{,}485.33$ coulombs, the charge of a mole of electrons.
- **Standard electrode potential.** The voltage of a half of a cell against a hydrogen electrode taken as zero, at standard concentrations.
- **Nernst equation.** $E_{cell} = E_{cell}^\circ - (RT/(nF)) \ln Q$, the voltage of a cell at the concentrations it has; zero in balance.
- **Fuel cell.** An electrochemical cell fed its reacting matter continuously, such as hydrogen and oxygen at 1.23 volts.
- **Bar.** A pressure of 100,000 pascals, about the pressure of the air.



Chapter 4

Gases, Liquids and Soft Matter

CHAPTER OVERVIEW

A phase of a substance is a form of it that is the same throughout, such as ice, liquid water or steam. A substance at a given temperature and pressure is found in the phase whose Gibbs free energy for each molecule is least, and in this chapter I follow that rule through the phases of ordinary matter. In a gas the molecules are far apart and move freely, and their strikes on a wall give a pressure P = nkT, the number of molecules in each unit of volume times the temperature as an energy, whatever the kind of molecule (Box 4.1). A real gas departs from this because its molecules take up room and pull on one another by the dispersion force. The van der Waals equation, the ideal gas law with both departures put in, gives a gas that becomes a liquid when squeezed below a definite temperature, the critical temperature, and passes into a dense fluid with no jump above it (Box 4.2). In a liquid the molecules touch, ordered over a few neighbors and disordered beyond. A liquid flows as its molecules pass over barriers to change neighbors, and its surface costs energy, the surface tension. The phase diagram maps where each phase is found. Its lines are where two phases have equal Gibbs free energies, and across each line a substance takes in a latent heat, the heat that changes its phase at a fixed temperature. That heat sets the slope of the line by the Clausius-Clapeyron relation (Box 4.3). Three lines meet at a triple point, and the line between liquid and gas ends at a critical point (Figure 4.1). Changes with a jump in energy are first-order changes. Changes in which

order grows from nothing, at a point fixed by a symmetry, are continuous changes. Where neither a jump nor a symmetry separates two arrangements, the change is a crossover, with no point. Water's hydrogen bonds raise its boiling point far above its heavier neighbors' and hold ice in an open framework with more than twice the room of close packing, so ice floats (Box 4.4). A liquid cooled too fast to find the rows of a crystal stops flowing with its disorder kept, and is a glass. Between solid and liquid lies soft matter, of four kinds. Polymers are long chains of small molecules joined end to end, and they pull back by counting when stretched (Box 4.5). Liquid crystals are made of rods that share a direction while they flow. Colloids are small particles kept scattered in a liquid or gas, set wandering by the uneven strikes of the molecules round them, which is Brownian motion. Gels are networks that hold a liquid. A gas whose atoms have come apart is a plasma. It cancels every charge beyond a short distance, its Debye length, and its electrons swing back and forth at a rate of their own, its plasma frequency.

I. Ice, Water and Steam

Chapter 3 ended with a question: molecules gather into gases, liquids and stranger things, so what are those?

Put a pan of ice cubes on a stove. The ice holds its shape, then slumps into water, which takes the shape of the pan, and the water at last boils away into steam, which fills the kitchen. The molecules are the same throughout, two hydrogen atoms joined to one oxygen atom, and only their arrangement has changed. Now look round the kitchen. Butter is firm in the refrigerator and soft on the table. A jelly wobbles and yet keeps its shape. Toothpaste stands up on the brush and still flows out of the tube. Soap turns grease and water into one milky wash. None of these is simply a solid or simply a liquid.

A *phase* of a substance is a form of it that is the same throughout, with one arrangement of its molecules, and that meets another phase of the same substance at a sharp boundary. Ice floating in water is two phases of

water side by side. The Ladder in Brief used the word in a second sense, for the stage of a wave's swing. In this chapter it always means a form of a substance. The three everyday phases are the solid, which keeps its shape, the liquid, which keeps its volume and takes the shape of what holds it, and the gas, which fills whatever holds it.

In Chapter 2 I found the rule that decides among them. A system held at a fixed temperature and a fixed pressure, as a pan on a stove is held by the room and the air, settles where its *Gibbs free energy*, $G = E + PV - TS$, is least. Here E is its energy, P the *pressure* (the force for each unit of area with which a gas or a liquid presses on what holds it), V its volume, T its temperature and S its entropy, the logarithm of the number of its arrangements. Ordered arrangements usually have less energy and less entropy than disordered ones, so order wins when cold and disorder when warm. And a change between arrangements is sharp, at one temperature, in the limit of many particles, only where a symmetry or a jump separates the arrangements. Where neither does, the change is a *crossover*, a smooth change with no jump. In this chapter I apply those results to the arrangements of ordinary matter.

So the reader's question is this: what are the phases of matter, and what lies between solid and liquid?

II. The Ideal Gas

Pump up a bicycle tire. Each push of the handle squeezes more air into the tire, and the tire grows harder, pressing back on the pump. Leave the bicycle out on a frosty night and the tire is softer in the morning, though no air has leaked out. What is the air doing to the tire, and why does the cold soften it?

Air is a gas of molecules, mostly nitrogen and oxygen, flying in every direction and striking whatever is in their way. Each molecule that strikes the inside of the tire bounces back and gives the wall a small push. The

pushes of the molecules, added over each square meter of the wall and each second, are the pressure of the air on the wall. More molecules in the same room give more pushes, and faster molecules give harder ones.

In a thin gas the molecules are far apart. At 300 kelvin and the pressure of the air, a cubic meter of any gas holds 2.45×10^{25} molecules (Box 4.1), so each has on average a cube 3.4 nanometers on a side to itself. In liquid water the molecules are packed 0.31 nanometers apart (computed from water's density, 997.05 kilograms for each cubic meter at 25 degrees Celsius, and its molar mass, the 18.015 grams that a mole of it weighs, Chapter 2, Section I). So the molecules of air are about eleven times farther apart than the molecules of a liquid, and they fill about a thousandth of the room they move in. They meet one another seldom, and between meetings each moves freely, as if the others were not there. A gas whose molecules are taken as points that exert no force on one another, except in the instant of a collision, is an *ideal gas*.

In Chapter 2, Section X, I found how much energy of motion such a molecule holds. By *equipartition*, each energy that goes as the square of a velocity holds on average ½kT, whatever the mass, where k is the Boltzmann constant and kT is the temperature written as an energy. Equipartition is all that the pressure needs. Box 4.1 contains the count.

Box 4.1. The pressure of a gas from the motion of its molecules

Premises. (1) A gas holds N molecules, each of mass m, in a box of volume V, so there are $n = N/V$ of them in each unit of volume; the molecules are taken as points that do not act on one another (an ideal gas). (2) A molecule that strikes a flat wall square to the direction x, with velocity v_x along x, bounces back with velocity $-v_x$, so it gives the wall the momentum $2mv_x$; momentum is mass times velocity, and the force on the wall is the momentum it receives in each second (standard mechanics). (3) By equipartition, the energy of motion along x, $\frac{1}{2}mv_x^2$, holds on average ½kT, so the average of mv_x^2 over the molecules is kT (Chapter 2, Section X).

Steps. Take the molecules with a given velocity v_x toward the wall, n_v of them in each unit of volume. In one second those within a distance v_x of the wall reach it, so $n_v v_x$ of them strike each unit of its area, and by (2) they give it the momentum $2mv_x \times n_v v_x = 2n_v mv_x^2$. Summing over every velocity toward the wall, which is half of all the velocities, the force on each unit of area is n times the average of mv_x^2, the factor 2 and the half canceling. By (3), that is $P = nkT$. With $n = N/V$, $PV = NkT$; for a mole of gas, N is the Avogadro constant N_A, and $PV = RT$, with $R = N_A k = 8.314$ joules for each kelvin and each mole, the gas constant of Chapter 3.

Result. The pressure of an ideal gas is $P = nkT$: the number of molecules in each unit of volume times the temperature as an energy, whatever the kind of molecule. At 101,325 pascals, the standard atmosphere (a pascal being one newton on each square meter, Chapter 2, Section XIV), and 300 kelvin, $n = P/kT = 2.45 \times 10^{25}$ molecules in each cubic meter; a mole of any gas fills 22.41 liters at 0 degrees Celsius and 24.47 liters at 25 degrees (computed).

The relation $PV = NkT$ is the *ideal gas law*. It says why the tire is soft in the morning: the air in it has the same number of molecules, and at the lower temperature each strikes the wall more gently. It says why the pump grows harder to push: squeezing the same molecules into less room raises n, and with it the pressure. And it says something the bicycle does not show: equal volumes of any two gases, at one temperature and one pressure, hold equal numbers of molecules, because the mass of a molecule does not enter. A heavy molecule moves more slowly than a light one at the same temperature, and the two strike the wall with the same average push.

So we now know what a gas is: molecules far apart, each moving freely, and pressing on their container by striking it, with a pressure set by their number and their temperature alone. A gas is the simplest phase, and the starting point for every other phase.

III. Real Gases and the Critical Point

Shake a canister of camping gas and something sloshes inside. The canister holds butane, which boils at about 0 degrees Celsius under the pressure of the air, so in an open room it is a gas (NIST Chemistry WebBook, butane, the average of its measured boiling points, 273 ± 1 kelvin). Squeezed into the canister, most of it has become a liquid. At 25 degrees Celsius the liquid holds the gas above it at about 2.4 times the pressure of the air (computed from the measured vapor pressures of Das, Reed and colleagues, 1973, as the NIST Chemistry WebBook fits them). An ideal gas could never do that: by Box 4.1, squeezing it only raises its pressure, without end. What does a real gas have that an ideal gas lacks?

A real gas has two things that an ideal gas lacks, and both things come from the molecules themselves. First, a molecule takes up room: two molecules cannot be pressed into the same place, because the electrons of each push back on the electrons of the other when they overlap. So the room open to each molecule is the volume of the box less the room the other molecules fill. Second, molecules pull on one another when they come close. Every two atoms or molecules attract by the *dispersion force*, a weak pull (in Volume One, Chapter 11, I derive it, and find that it acts between all atoms and molecules). It arises because the electrons of each, at any moment, sit a little off center, and each such passing separation of charge in one induces a matching one in the other, so that the two attract. That pull slows a molecule as it nears the wall, since the molecules behind it hold it back, and so it lowers the pressure. And it is strongest where the molecules are crowded.

Johannes Diderik van der Waals put the room and the pull into the ideal gas law in his doctoral thesis of 1873 (van der Waals, 1873). For a mole of gas in a volume V_m, the room lost to the molecules is a constant b. The lowering of the pressure by the pull goes as the square of the number of molecules in each unit of volume, a/V_m^2, with a a second constant. It

goes as the square because each molecule's pull on its neighbors grows with their number, and the number of molecules feeling it grows too. Put into the ideal gas law, the two corrections give the pressure raised by a/V_m^2, times the room less b, equal to RT:

$(P + a/V_m^2)(V_m - b) = RT.$

The ideal gas law with the two corrections is the *van der Waals equation*. When the gas is thin, V_m is far larger than b and a/V_m^2 is far smaller than P, and the equation is the ideal gas law again. When the gas is squeezed and cool, the two terms take over, and the equation does what the ideal gas law cannot. Below a definite temperature, it gives a gas that, squeezed far enough, falls together into a liquid. Above that temperature, squeezing only makes the gas denser, with no jump.

Thomas Andrews found that temperature for carbon dioxide (Andrews, 1869). He sealed liquid carbon dioxide with its gas in a strong glass tube and warmed it. The surface between liquid and gas grew faint as the temperature rose, and near 31 degrees Celsius it vanished. Above that temperature, at every pressure he could apply, the tube held one fluid with no surface. He named the point where the surface vanishes the critical point. In Chapter 2, Section XV, I gave the *critical point* as the temperature and pressure above which liquid and gas pass into each other with no jump. In Box 4.2 I find it in the van der Waals equation.

Box 4.2. The critical point

Premises. (1) A mole of gas follows $P = RT/(V_m - b) - a/V_m^2$, the van der Waals equation solved for the pressure, with a and b positive constants of the gas. (2) A phase can last only where squeezing it raises its pressure, so that P falls as V_m grows at a fixed temperature; where the equation gives the opposite, the phase is not stable, and the gas divides into a liquid and a gas side by side, at the one pressure where the two have equal Gibbs free energies for each molecule (standard thermody-

namics, with Chapter 2, Section XIV). (3) Measured, carbon dioxide's critical point lies at 304.13 kelvin and 7.377 million pascals, with a mole filling 94.12 cubic centimeters there (Span and Wagner, 1996).

Steps. At high temperature the first term of (1) rules, and P falls steadily as V_m grows, as for an ideal gas. At low temperature the second term pulls the curve down at middle volumes, and P first falls, then rises, then falls again as V_m grows; on the rising part, by (2), the gas divides into liquid and gas. Between the two there is one temperature at which the fall, the rise and the fall merge into one point where the curve is flat and bends neither way: there $dP/dV_m = 0$ and $d^2P/dV_m^2 = 0$. Solving those two conditions with (1) gives $V_c = 3b$, $T_c = 8a/(27Rb)$ and $P_c = a/(27b^2)$ (mathematics). So the ratio $P_cV_c/(RT_c)$ is $3/8 = 0.375$ for every gas that follows the equation, whatever its a and b. By (3), the ratio for carbon dioxide is $7{,}377{,}298 \times 94.12 \times 10^{-6}/(8.314 \times 304.13) = 0.275$ (computed).

Result. Below the critical temperature $T_c = 8a/(27Rb)$, a gas squeezed far enough becomes a liquid, with a jump in density at the pressure where the two phases have equal Gibbs free energies; above it, the gas passes into a dense fluid with no jump at any pressure. The two kinds of departure from the ideal gas, the room the molecules fill and their pull, are enough to make the critical point. The equation gives the critical point and the form of the curves. For carbon dioxide the measured ratio is 0.275 against the equation's 0.375, so the exact values for each gas come from measurement, tabulated for carbon dioxide by Roland Span and Wolfgang Wagner (1996) and for water by Wolfgang Wagner and Andreas Pruß (2002).

Above its critical point a substance is a *supercritical fluid*, a fluid whose density can be raised smoothly from that of a gas to that of a liquid by squeezing, with no boiling on the way and no surface between two parts. The smooth change from gas to liquid above the critical point is the plainest case of the crossover of Chapter 2. Below the critical point, liquid and gas differ by a jump in density and in energy for each molecule, and the jump is what makes boiling happen at one temperature for each pressure. At the critical point the jump shrinks to nothing, and beyond it neither a

jump nor a symmetry separates the two arrangements. Near the critical point the fluid hovers between the two densities. The density at each place wanders far from its average over regions large enough to scatter light, so that a clear fluid near its critical point turns milky. That milkiness is called *critical opalescence*. It is the *fluctuations* of Chapter 2, the small, ever-changing differences of a system's macrostate from the most probable one, which the motion of its particles makes, grown large enough to see.

IV. Liquids

Pour a bag of marbles into a bowl and shake it gently. The marbles lie touching one another, each nested among its neighbors, with no rows and no pattern. Shaken, they slide past one another and the heap flows, yet it stays in a heap at the bottom of the bowl, where a gas would fill a box. A liquid is like that, and the picture describes most of what a liquid is.

In a liquid the molecules touch. A liquid is nearly as dense as its solid. Most substances are a little less dense as liquids than as solids, and water, denser than its ice, is the famous exception (Section VI). Each molecule is held by its neighbors, by the dispersion force and by whatever stronger pulls its kind of molecule makes, and that is why a liquid keeps its volume. But the neighbors keep changing places. In X-ray and neutron scattering, experimenters send waves through a liquid and record how they are bent by the molecules. They find that each molecule has a ring of neighbors at nearly the distance a solid would give them, a second ring less sharply placed, and a third barely marked, after which the arrangement is random (for liquid argon, Yarnell, Katz, Wenzel and Koenig, 1973). Rings of neighbors that fade after the third ring are order over a few neighbors and none beyond: *short-range order*, the arrangement of a molecule's nearest neighbors, held for a few molecular distances and lost over longer ones. A crystal, Chapter 5 will show, has order without end.

A liquid flows because its molecules change neighbors. To slip out of the ring that holds it, a molecule must push its neighbors aside for a moment, which needs energy. So changing neighbors is a passing over a barrier, of the kind I counted in Chapter 3, and it happens at a rate that rises steeply with temperature. How hard a liquid must be pushed to make it flow at a given speed is its *viscosity*, its thickness against flowing, and it falls steeply as the liquid is warmed, because the molecules cross their barriers more often. The steep fall of a liquid's viscosity as the liquid is warmed is why syrup pours freely when hot and slowly when cold. The same steep change is why a liquid cooled far enough can stop flowing altogether, as I show in Section VII.

A liquid also has a surface, and the surface has a cost. Lay a steel paper clip flat on still water and it floats, though steel is far denser than water. The water's surface dimples under it like a stretched sheet. Water striders walk on ponds for the same reason, and a drop of water hanging from a tap pulls itself round. A molecule inside a liquid is held on every side by its neighbors. A molecule at the surface has neighbors on one side only, so it lacks part of what holds the molecules inside, and bringing a molecule from the inside to the surface costs energy. The energy it takes to make one more unit of area of surface is the liquid's *surface tension*. It is also the force with which the surface pulls along each unit of length of any line drawn on it. For water at 25 degrees Celsius it is 71.97 thousandths of a joule for each square meter (International Association for the Properties of Water and Steam, 2014).

The size of the surface tension can be understood from the molecules. A water molecule at the surface fills about $(0.31 \text{ nanometers})^2$ of it, so the surface tension gives each surface molecule an extra energy of about 0.043 eV (computed), an electron volt being the energy an electron gains in passing through a voltage of one volt. Boiling, Section V will show, takes 0.42 eV for each molecule, the whole of what holds a molecule in the liquid. So the surface costs each molecule there about a tenth of the binding that boiling removes entirely. Since the surface costs energy, a liquid left to

itself makes its surface as small as it can for its volume. The shape with the least surface for a given volume is the sphere (mathematics), so a falling raindrop is round, and so is a drop of oil in water.

So we now know what a liquid is: molecules touching, held by their neighbors, ordered over a few neighbors and disordered beyond, changing neighbors by crossing barriers, and paying a cost at their surface.

V. The Map of the Phases

A pressure cooker cooks potatoes far faster than an open pan. It holds the steam in, so that the pressure inside rises to about twice the pressure of the air. At that pressure water boils at about 121 degrees Celsius in place of 100 (computed from the measured boiling curve of water, International Association for the Properties of Water and Steam, 1992). So the water inside, and the potatoes, are hotter, and the reactions of cooking go faster, steeply so, as I found in Chapter 3 for every route over a barrier. The boiling point of water is a temperature for each pressure. Where, for each temperature and each pressure, is a substance a solid, a liquid or a gas?

In Chapter 2 I gave the answer in one rule: at each temperature and each pressure, the substance is found in the phase whose Gibbs free energy for each molecule is least. Each phase has its own Gibbs free energy, which changes smoothly with temperature and pressure. Where two phases have equal Gibbs free energies, the two are found side by side, as ice and water are at the melting point, and the points where that happens form a line across the map of temperature and pressure. On one side of the line one phase is found, on the other side the other. Such a map, of the phases of a substance against temperature and pressure, is its *phase diagram*, and Figure 4.1 draws water's.

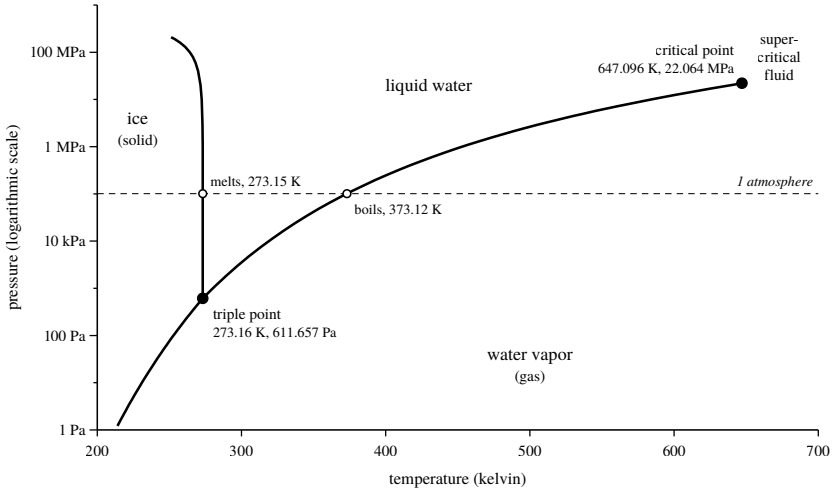


Figure 4.1. The phase diagram of water: pressure, on a scale in which each mark is a hundred times the last, against temperature in kelvin. The curves are computed from the equations of the International Association for the Properties of Water and Steam for the boiling curve (1992), the curve along which ice passes straight to vapor, and the melting curve of ordinary ice (2008). The three curves meet at the triple point, 273.16 kelvin and 611.657 pascals. The boiling curve ends at the critical point, 647.096 kelvin and 22.064 million pascals, beyond which liquid and vapor are one supercritical fluid. The dashed line is the pressure of the air, 101,325 pascals: on it ice melts at 273.15 kelvin and water boils at 373.12 kelvin. The melting curve leans backward, to lower temperatures at higher pressures, up to 208.6 million pascals at 251.165 kelvin, where other forms of ice, found only under pressure, take over (not drawn).

The map has three lines. The boiling curve divides liquid from gas, the melting curve divides solid from liquid, and a third curve divides solid from gas, where ice passes straight to vapor without melting. That passing straight from solid to gas is *sublimation*, and it is how snow on a cold, dry, sunny day can vanish without ever turning to water. The three lines meet

at one point, the *triple point*, the one temperature and pressure at which solid, liquid and gas are found together: for water, 273.16 kelvin and 611.657 pascals. The boiling curve ends at the critical point of Section III.

Crossing a line takes something. Melting ice in a glass of water, stirred, stays at one temperature until the last of it has melted (Chapter 2, Section XV), and all the while the glass takes in heat from the room. The heat that a substance takes in to pass from one phase to the other at a fixed temperature and pressure is its *latent heat*. For water it is 333.55 kilojoules for each kilogram to melt, which is 6.01 kilojoules for each mole. To boil at its boiling point under the pressure of the air, water takes 40.65 kilojoules for each mole (*CRC Handbook of Chemistry and Physics*, 62nd edition, 1981, CRC being the name of its publisher). The two phases have equal Gibbs free energies, E + PV − TS, where they meet, so the heat taken in at fixed pressure, the change of E + PV, equals T times the change of S. So the latent heat L, for each molecule, equals the temperature times the jump in entropy: L = TΔS, with ΔS, read "delta S", the entropy of the warmer phase less that of the colder. For water boiling, ΔS is 13.1 times k for each molecule, and for ice melting it is 2.6 times k (computed). Turning liquid into gas multiplies the number of arrangements open to each molecule far more than turning solid into liquid does, because the gas gives each molecule more than a thousand times the room the liquid gives it (Section II).

So there are two kinds of change from one phase to another. A change with a jump in energy and entropy for each molecule, and so with a latent heat, is a *first-order change*: melting, boiling and sublimation are first-order changes. A change in which the order grows from nothing at one point, with no jump and no latent heat, is a *continuous change*. It happens at a point because a symmetry separates the ordered arrangement from the disordered one, as at the Curie point of a magnet, where the spins of iron's atoms choose a direction (Chapter 8). Both are sharp, at one temperature for each pressure, in the limit of many particles, because something separates the arrangements: a jump in the first case and a symmetry in the second. Where neither separates them, the change is a crossover,

smooth and at no one point, as above water's critical point. The critical point itself is where a first-order change ends: the jump shrinks to nothing as the boiling curve is followed up to it, and at the critical point the liquid and the gas become one fluid continuously.

How steeply does a line on the map rise? The answer is in what the two phases differ by, as Box 4.3 shows.

Box 4.3. The slope of a line on the map

Premises. (1) Along a line of the phase diagram the two phases have equal Gibbs free energies for each molecule, $g_1 = g_2$, at every point of the line (Chapter 2, Section XIV). (2) For one phase, a small change dT of temperature and dP of pressure changes its Gibbs free energy for each molecule by $dg = v\,dP - s\,dT$, where v and s are its volume and entropy for each molecule (standard thermodynamics: $G = E + PV - TS$, with the change of energy $dE = T\,dS - P\,dV$; the heat taken in is T dS, since heat Q taken in at temperature T carries the entropy Q/T, and the work given out in swelling by dV against the pressure P is P dV and carries no entropy, as Chapter 2, Box 2.2, premise (3), found). (3) The latent heat for each molecule is $L = T(s_2 - s_1)$ (this section).

Steps. Moving along the line from one point to the next, g_1 and g_2 change by the same amount, by (1); so $v_1\,dP - s_1\,dT = v_2\,dP - s_2\,dT$, by (2). Gather the terms: $(s_2 - s_1)\,dT = (v_2 - v_1)\,dP$, so $dP/dT = (s_2 - s_1)/(v_2 - v_1)$. By (3), $dP/dT = L/(T\Delta v)$, with Δv the change of volume for each molecule. The relation just found for the slope of the line along which two phases stand together is the *Clausius-Clapeyron relation* (Clapeyron, 1834; Clausius, 1850). For boiling, the gas has far more volume than the liquid, so Δv is close to the gas's own volume kT/P (Box 4.1), and $dP/dT = LP/(kT^2)$; taken over a range in which L changes little, this gives $\ln(P_2/P_1) = -(L/k)(1/T_2 - 1/T_1)$. With L = 40.65 kilojoules for each mole, water boils where the air presses at 70,000 pascals, about seven tenths of its pressure at sea level, at 89.7 degrees Celsius; the measured boiling curve gives 89.9 (computed from International Association for the Properties of Water and Steam, 1992).

Result. The slope of a line on the phase diagram is the latent heat over the temperature times the change of volume: $dP/dT = L/(T\Delta v)$. A boiling curve always rises steeply with temperature, since the gas takes far more room than the liquid. A melting curve rises where the liquid takes more room than the solid, which is the usual case, and leans backward where the liquid takes less, which is the case of water (Box 4.4).

Carbon dioxide shows the map from another side. Its triple point lies at 216.59 kelvin and 518,000 pascals, about five times the pressure of the air (Span and Wagner, 1996). At the pressure of the air, then, carbon dioxide has no liquid at any temperature: the line it crosses when it warms is the line between solid and gas, and solid carbon dioxide, dry ice, passes straight into gas without melting. So we now know what the map of the phases holds. It has lines where two phases have equal Gibbs free energies, a latent heat across each line that sets its slope, a point where three meet, and a point where the line between liquid and gas ends.

VI. Water

In winter a lake freezes from the top down. The ice forms a lid on the water, the fish swim on beneath it, and a bottle of water left in a freezer cracks as its water turns to ice and swells. Almost every other liquid shrinks as it freezes, and its solid sinks in it. Water is unusual in this, and in more. Its molecule is light, and yet it boils at 100 degrees Celsius, far hotter than molecules of its size and kind. Why is water so unlike its neighbors?

The answer is one kind of bond. A water molecule is an oxygen atom joined to two hydrogen atoms, each by a *covalent bond*, a bond made by a pair of electrons shared between two atoms (Volume One, Chapter 11). Oxygen pulls the shared electrons toward itself, so each hydrogen is left a little positive and the oxygen a little negative. The oxygen also carries two *lone pairs*, pairs of its outer electrons that take no part in its bonds and

stand out from the far side of the atom. A hydrogen of one water molecule, left a little positive, is pulled toward a lone pair of the oxygen of another. That pull is a *hydrogen bond*: the attraction between a hydrogen atom bound to a strongly electron-pulling atom, such as oxygen, nitrogen or fluorine, and a lone pair of another such atom. In Volume One, Chapter 11, I find that it lies between the other two in strength: stronger than the dispersion force, and weaker than a covalent bond. Each water molecule has two hydrogens to give and two lone pairs to take, so it can make up to four hydrogen bonds, pointing out from it toward the four corners of a tetrahedron, a solid with four triangular faces.

The boiling point shows the hydrogen bond at work first. The molecules made of hydrogen with oxygen's heavier cousins in the periodic table, sulfur, selenium and tellurium, each with two hydrogen atoms as water has, boil at −60.3, −41.3 and −4 degrees Celsius (Greenwood and Earnshaw, 1997). Each is held to its neighbors chiefly by the dispersion force, which grows with the number of electrons a molecule has, so the heavier the molecule, the higher it boils. Water's molecule is the lightest of the four, and on that trend it would boil lowest of all, below −60 degrees. It boils at 100 degrees. Boiling takes 40.65 kilojoules for each mole of water (Section V), 0.42 eV for each molecule, thirteen times kT at the boiling point (computed). The 0.42 eV that boiling takes for each molecule is the energy of the hydrogen bonds a molecule leaves behind when the molecule goes free, added to the molecule's dispersion pull. The same bonds give water its large surface tension (Section IV) and its large heat capacity (Chapter 2, Section VII), since heat that would speed the molecules goes first into loosening their bonds.

Ice shows the hydrogen bond at work a second way. In ice every molecule makes all four of its hydrogen bonds, and the four neighbors stand at the corners of a tetrahedron round it. That arrangement is open. Four neighbors at those angles leave a great deal of empty room between them, far more than a crowd of molecules jostling at the same distance would. In Box 4.4 I count the room.

Box 4.4. Why ice floats

Premises. (1) In ice each water molecule is joined by hydrogen bonds to four neighbors at the corners of a regular tetrahedron round it, the centers of neighboring oxygen atoms lying $d = 0.276$ nanometers apart (Petrenko and Whitworth, 1999). (2) In an arrangement of points in which every point has four neighbors at the corners of a regular tetrahedron at distance d, each point has to itself a volume $8d^3/(3\sqrt{3})$ (mathematics: the arrangement of the carbon atoms in diamond, which ordinary ice matches in its count of neighbors and its distances). (3) In an arrangement of balls of diameter d packed as closely as balls can be, each ball touching twelve others, each ball has to itself a volume $d^3/\sqrt{2}$ (mathematics). (4) A water molecule has a mass of 18.015 atomic mass units, the atomic mass unit being a twelfth of the mass of an atom of carbon-12, 1.66054×10^{-27} kilograms (the value recommended in 2022 by the Committee on Data of the International Science Council, CODATA). (5) Measured at 0 degrees Celsius and the pressure of the air, ice has a density of 916.7 kilograms for each cubic meter and liquid water 999.84 (*CRC Handbook of Chemistry and Physics*, 97th edition, Harvey, 2017).

Steps. By (1) and (2), each molecule in ice has $8 \times 0.276^3/(3\sqrt{3}) = 0.0324$ cubic nanometers to itself, and by (4) the density of ice is 2.99×10^{-26} kilograms over 3.24×10^{-29} cubic meters, 924 kilograms for each cubic meter; the measured value is 916.7 (computed). By (3), the same molecules packed as closely as balls, at the same distance, would have 0.0149 cubic nanometers each, a density of 2,012: the tetrahedral bonds of ice give each molecule more than twice the room that close packing would. When ice melts, a share of the hydrogen bonds break, the open framework partly falls in, and molecules move into some of its empty room, so the liquid is denser: by (5), water at 0 degrees is 9.1 percent denser than ice, and ice is 8.3 percent less dense than water. In Box 4.3, the change of volume on melting, Δv, is then negative, and with the latent heat of 333.55 kilojoules for each kilogram (Section V), $dP/dT = L/(T\Delta v) = -13.5$ million pascals

for each kelvin: the melting point falls by 0.0075 kelvin for each added atmosphere of pressure (computed; the measured melting curve of Figure 4.1 gives the same).

Result. Ice is less dense than liquid water because each of its molecules holds four neighbors at the corners of a tetrahedron by hydrogen bonds, an open arrangement with more than twice the room of close packing; melting breaks part of that framework and lets the molecules crowd closer. So ice floats, with 91.7 percent of its volume below the surface of fresh water (916.7/999.84), and water's melting point falls as the pressure rises, which is why the melting curve of Figure 4.1 leans backward.

The open framework goes gradually when ice melts. Just above 0 degrees Celsius liquid water still holds many open patches of hydrogen-bonded molecules, and as the water warms they keep breaking and the molecules keep crowding closer. Meanwhile the faster motion of warming pushes the molecules apart, as it does in every liquid. The crowding wins up to about 4 degrees, the pushing apart above it, so water is densest near 4 degrees Celsius, at 999.97 kilograms for each cubic meter (as tabulated by the Engineering ToolBox). A lake cooling in autumn therefore turns over until all of it is near 4 degrees. Below that, the colder water stays on top and freezes there, and the ice lid keeps the deep water liquid. So we now know why water is unlike its neighbors. Its hydrogen bonds hold its molecules far more strongly than its small size would suggest, which raises its boiling point, and in the solid they hold the molecules apart in an open framework, which makes ice float.

VII. Glass

Boil sugar with a little water until it is very hot, and pour it onto a cold slab. It sets hard and clear: a boiled sweet, as smooth and glassy as a window. Boil the same sugar with butter and milk, beat it as it cools slowly,

and it sets soft and grainy: fudge, whose grains are tiny crystals of sugar. The same molecules made two solids, and the speed of cooling determined which one formed.

In Chapter 2 I found that a system cooled too fast to reach its arrangement of least energy keeps the arrangement it was caught in. A crystal, the arrangement in rows of Chapter 5, is what a liquid of sugar or of silica would settle into if it were given time. To build it, molecules must leave their jumbled places in the liquid and take up places in rows, and each such move is a passing over a barrier (Section IV), at a rate that falls steeply as the liquid cools (Chapter 3). Cool the liquid slowly and the molecules find the rows: the liquid crystallizes at its melting point. Cool it fast and it passes its melting point still a liquid, a *supercooled liquid*, one held below its melting point without crystallizing. As it cools further its viscosity rises steeply, and at last its molecules change places so seldom that, on any time anyone could wait, the liquid has stopped flowing. It is then a *glass*: a solid whose molecules are caught in the disordered arrangement of a liquid. A solid with no repeat in its arrangement is called *amorphous*, meaning without form, and a glass is the commonest kind.

The temperature at which a cooling liquid becomes a glass is its *glass transition* temperature. It is usually marked where the viscosity reaches about 10^{12} pascal seconds, the pascal second being the unit in which viscosity is measured. Edgar Zanotto gives the viscosity of a solid glass as at least 10^{12} to 10^{13} pascal seconds (Zanotto, 1998). For the flat glass of windows, made mostly of silica with soda and lime, the glass transition lies near 564 degrees Celsius (Seward and Vascott, 2005). The glass has the same disordered arrangement that the liquid had, so neither a symmetry nor a jump separates the two: the glass is the liquid's arrangement stopped. So, by the rule of Chapter 2 for sharp changes, the glass transition happens over a range of temperature, where the changes of phase of Section V happen at a point. Where in that range the liquid stops depends on how fast it was cooled. A liquid cooled faster is caught sooner, at a higher temperature.

Below its glass transition a glass holds its shape over every human scale of time. Zanotto worked out from the viscosity of the glasses of old cathedral windows that their time to relax and flow at room temperature is "well beyond the age of the Universe" (Zanotto, 1998). So the old windows that are thicker at one edge were made unevenly, and they have kept the shape they were made in. A glass keeps a residual entropy, the entropy of the jumbled arrangement it was caught in (Chapter 2, Section XVI). It conducts heat poorly, a few hundred times less well than copper, because its disorder scatters the vibrations that carry heat through a crystal (Chapter 5, Section V). So we now know what a glass is: a liquid cooled too fast to find its rows, its disordered arrangement kept, and solid because its molecules change places too seldom for any wait to show it.

VIII. Chains, Rods and Particles

Return to the kitchen. A bowl of cooked spaghetti, a dish of jelly, a carton of milk and a bar of soap are each made of pieces far larger than a molecule: long chains, networks, droplets. And each gives under a small push. Matter whose structures are large against single molecules and held together by weak forces, so that it yields to a gentle push and is reshaped by the jostling of heat at ordinary temperatures, is called *soft matter*. Four kinds of it fill the space between solid and liquid.

The first kind is made of chains. A *polymer* is a molecule made of many small molecules, its *monomers*, joined end to end by covalent bonds into a long chain. Polyethylene is a chain of many thousands of units of two carbon atoms each, every carbon carrying two hydrogens. Such a chain is like a strand of cooked spaghetti, able to bend at each joint, and in a melt or a solution the motion of heat bends it every way at once. How big is a chain of N links? If each link pointed along the last, the chain would be N links long. But each link points in a direction that the others leave free, and the far end wanders from the near one as a walker taking N steps in directions chosen at random wanders from his starting point. Such a walker

ends, on average, about $\sqrt{N}$ steps from where he began (mathematics), so a chain of ten thousand links is only about a hundred links across. The chain is a loose ball, mostly empty and threaded through by other chains. Paul Flory set out this picture of the chain, and the pull of stretched rubber that follows from it, in his account of how such chains behave in a melt and in solution (Flory, 1953).

Pull on the two ends of such a chain and it pulls back, and the pull comes almost wholly from counting. A chain with its ends far apart can take far fewer shapes than one whose ends are close, so stretching it lowers its entropy, and by Chapter 2 a system at a fixed temperature resists any change that lowers its entropy without lowering its energy. In Box 4.5 I find the pull.

Box 4.5. A chain pulls back by counting

Premises. (1) A polymer chain is taken as N links of length b, each free to point in any direction whatever the others do, and the energy of the chain is the same for every shape it takes (standard model of a flexible chain). (2) For large N, the number of shapes in which the far end lies at a given place a distance r from the near end is in proportion to $e^{-3r^2/(2Nb^2)}$, and the average of r^2 over all shapes is Nb^2 (mathematics: the sum of many independent steps of random direction). (3) At a fixed temperature T, the free energy $F = E - TS$ is least, and the force needed to hold the ends a distance r apart is the change of F with r, dF/dr (Chapter 2, Section XIV; standard thermodynamics). (4) The entropy is $S = k \ln W$, with W the number of shapes (Chapter 2, Section III).

Steps. By (2) and (4), the entropy of the chain with its ends r apart is $S(r) = S(0) - 3kr^2/(2Nb^2)$. By (1), the energy does not change with r, so by (3) $F(r) = F(0) + 3kTr^2/(2Nb^2)$. So the force needed to hold the ends r apart is $f = dF/dr = 3kTr/(Nb^2)$, and the chain pulls back with that force.

Result. A flexible chain is a spring whose pull comes from its entropy: the pull grows in proportion to the stretch, and it grows in proportion to the temperature, since the temperature sets how much each lost arrangement costs. A chain of N links has a typical size $b\sqrt{N}$.

Rubber is a tangle of such chains joined to one another at scattered points, so that the whole piece is one network, and its stretchiness is the pull of Box 4.5 added over all its chains. Two things follow that set rubber apart from an ordinary spring. A stretched rubber band pulls harder when it is warmed, since its pull is in proportion to the temperature, and so a weight hung on a rubber band rises when the band is heated. And a rubber band stretched quickly warms up, as anyone can feel by stretching one against the lips. The stretch lowers the entropy of the chains' shapes, and it is too fast for heat to leave. So the entropy appears instead in the faster jostling of the atoms, which is a higher temperature. A glass and a polymer meet in plastics, which I take up in the section In Use. Below its own glass transition a melt of chains is a stiff plastic, and above it, a soft and pliable one.

The second kind is made of rods. Logs floated down a river all point downstream, though they are not arranged in rows. Some molecules are long and stiff, like rods, and in a range of temperatures between their solid and their liquid they do the same. They flow as a liquid does, while their long axes point, on average, along one shared direction. Such a phase is a *liquid crystal*, and the simplest kind, in which the rods share a direction and nothing else, is called *nematic*, from the Greek for thread. Friedrich Reinitzer found the first in 1888, in cholesteryl benzoate, a substance made from cholesterol, which melted at 145.5 degrees Celsius into a cloudy liquid and turned clear at 178.5 degrees (Reinitzer, 1888). The cloudy liquid was the liquid crystal. Its rods, sharing a direction over regions large enough to scatter light, made it cloudy, and at 178.5 degrees they lost the shared direction and the liquid cleared. The clearing happens

at a point, by the rule of Chapter 2, because a symmetry separates the two arrangements: the liquid crystal picks out one direction and the clear liquid picks out none.

The third kind is made of particles. A *colloid* is a substance of small particles or droplets, each roughly between a billionth and a millionth of a meter across, held scattered through another substance without settling out (the range the International Union of Pure and Applied Chemistry gives). Milk is droplets of fat in water. Fog is droplets of water in air. Ink is fine grains of pigment in water. Look through a microscope at such grains and they are always moving: each jiggles and wanders. Robert Brown saw it in grains from pollen in water, and Albert Einstein explained it. Each grain is struck on every side by the molecules of the water, unevenly from moment to moment. By equipartition it holds the same average energy of motion as a molecule, three halves of kT, a half of kT for each of the three directions it can move in, however large it is (Einstein, 1905). That wandering is *Brownian motion*, and Jean Perrin's measurements of it confirmed Einstein's account, and with it the reality of molecules (Perrin, 1909). A colloid stays scattered because something keeps its particles from clumping. The dispersion force pulls any two of them together, and a like electric charge on their surfaces, or a coat of chains on each that keeps the next at a distance, pushes them apart.

The fourth kind is a network that holds a liquid. A *gel* is a network of chains or particles joined at points into one framework that reaches through the whole of a liquid and holds it in its gaps. A jelly is a gel of gelatin, chains of protein from the cooking of bones and skin, joined into a network as the warm liquid cools. It is mostly water, yet it holds its shape, because the network reaches from wall to wall of its dish and bears its weight. So we now know what lies between solid and liquid. There are chains that tangle and pull back by counting, rods that share a direction while they flow, particles held scattered in a liquid by a balance of pulls and pushes, and networks that hold a liquid in their gaps.

IX. Plasma

A neon sign glows red where an electric current passes through the thin gas in its tube. Lightning lights a path of air for an instant. In each, the gas has become something other than a gas of molecules: some of its atoms have lost electrons, and the free electrons and the charged atoms they left behind carry the current. What happens to a gas heated or driven so hard that its atoms come apart?

In Chapter 2, Box 2.4, I found where atoms and free electrons settle in balance. By Saha's rule, the free electrons win once the temperature, as an energy, is a modest share of the binding of the electron, because a free electron has so many more ways to be than a bound one. A gas in which a large share of the atoms have lost electrons is a *plasma*: a mixture of free electrons and *ions*, an ion being an atom or nucleus with a net charge. Irving Langmuir gave it its name in 1928: "We shall use the name plasma to describe this region containing balanced charges of ions and electrons" (Langmuir, 1928). The Sun and the other stars are made of plasma.

A plasma carries no net charge over any region of fair size, and the reason is that its charges arrange themselves round one another. Each positive ion draws the free electrons a little toward itself and pushes the other ions a little away, so that it gathers round itself a cloud with an opposite charge, and beyond that cloud its field is canceled. In a plasma, then, there are charges which gather round a charge and cancel its field at a distance. This canceling is called *screening*. The canceling reaches over a distance set by the balance between the pull of the charges and the jostling of heat, which keeps them from gathering too closely. That distance is the *Debye length*, $\sqrt{(\varepsilon_0 kT/(ne^2))}$ (Debye and Hückel, 1923). Here n is the number of electrons in each unit of volume, e the size of the electron's charge, and ε_0 the electric constant, the number that sets, in the international units, how strong a field a given charge makes. In words, the Debye length grows

with the temperature and shrinks as the electrons crowd closer. Seen from farther away than the Debye length, every charge in a plasma is canceled by its cloud.

A plasma also rings. Push all its electrons a small distance x to one side, leaving the heavy ions where they were. One face of the plasma is now left with a sheet of positive charge and the other with a sheet of negative charge, and the field between the two sheets is nex/ε_0 (standard electromagnetism), which pulls each electron back with the force ne^2x/ε_0. A pull back in proportion to the distance makes a swing, as a spring does, and the electrons swing back and forth through the ions at the angular frequency, the number of swings in each second times 2π,

$\omega_p = \sqrt{(ne^2/(\varepsilon_0 m_e))}$,

read "omega p", with m_e the electron's mass. Dividing by 2π gives the number of swings in each second. The number of swings in each second is the *plasma frequency*, and the plasma frequency is set by the number of free electrons in each unit of volume, by the electrons' charge and mass, and by nothing else. The upper atmosphere is a plasma, made by the Sun's ultraviolet light, light of shorter wavelength than the violet the eye can see. It holds about 10^{12} free electrons in each cubic meter at its densest (German Aerospace Center, Ionosphere Monitoring and Prediction Center), and its plasma frequency is then 9.0 million swings in each second (computed). Radio waves of lower frequency than that are sent back by it, because its electrons swing in time with them. Short-wave radio reaches round the curve of the Earth by being sent back from the upper atmosphere. In Chapter 11 I take up what the plasma frequency does to light in matter, and why metals, whose free electrons are far denser, send back visible light.

So we now know what a plasma is: a gas whose atoms have come apart into ions and free electrons, which cancels any charge in it beyond the Debye length and rings at a frequency set by its density of electrons.

In Use

Plastics are polymers shaped above their glass transition and used below it. The clear bottles of soft drinks are polyethylene terephthalate, whose chains pass their glass transition between 70 and 85 degrees Celsius (NETZSCH, polymer database). The bottle is blown from a warm, soft tube of it and cooled quickly, so that its chains are caught jumbled, as a glass. So the bottle stays clear and tough (NETZSCH: amorphous polyethylene terephthalate is used "mainly" for bottles, for its "high transparency and resistance to breaking"). Fill such a bottle with water near boiling and it slumps, because it has been carried above its glass transition and its chains can move again. A car tire is the other kind of polymer at work: chains joined into one network, which pull back by the counting of Box 4.5 each time the tire is pressed flat against the road.

Liquid-crystal displays use the shared direction of a nematic liquid. A thin layer of it lies between two plates of glass whose inner surfaces are treated so that the rods next to each plate lie along a set direction. The two directions are a quarter turn apart, so the rods twist by a quarter turn through the layer. The twisted layer turns the light passing through it, and a voltage across the layer turns the rods to lie along the electric field, which undoes the twist (Schadt and Helfrich, 1971). With filters on each side that pass light of one direction of vibration, which I explain in Chapter 11, each small region of the screen then turns light on or off as its voltage is switched. The rods can be turned by a volt or two, since they are held in place only by the weak shared direction of a liquid crystal, far more weakly than the bonds of a solid hold its atoms. A mixture made in 1972 reached nine tenths of its full darkening at 1.4 volts (Boller, Scherrer, Schadt and Wild, 1972).

Soap works by joining two things that will not mix. A soap molecule is an *amphiphile*, a molecule with one end drawn to water and the other end shunning it. It has a charged head, which water's molecules gather round,

on a long tail of carbon and hydrogen, which water's hydrogen bonds push out of their way. In water, above a small concentration, the molecules gather into balls with their tails inward and their heads outward, called *micelles* (standard colloid chemistry). For one common soap, sodium dodecyl sulfate, they form above about 0.008 moles in each liter (Mukerjee and Mysels, 1971). Grease dissolves in the oily middle of a micelle and is carried off in the water, and the washing water, full of micelles, is a colloid (standard colloid chemistry).

Plasma lights a fluorescent lamp. A current through the thin mercury vapor in the tube drives free electrons into the mercury atoms, which give off ultraviolet light at 253.7 and 185.1 nanometers, carrying some 63 percent of the energy put in. A powder on the inside of the glass takes in that ultraviolet light and gives out visible light (Lamptech, "Fluorescent Lamp Operation"). At the other extreme of plasma, a machine for fusion must hold a plasma of hydrogen's heavier forms hot enough for their nuclei to strike one another and join. Inside ITER, the international machine for fusion now being built, the plasma "must reach 150 million °C, or ten times the temperature at the core of the Sun" (ITER Organization). At that temperature kT is 12.9 thousand electron volts (computed), nearly a thousand times hydrogen's binding of 13.6 eV, so every atom is stripped bare. Any wall the plasma touched would cool it, so it is held away from the walls by magnetic fields, which bend the paths of its charged particles into loops.

Summary

A phase is a form of a substance the same throughout, with one arrangement of its molecules, and at each temperature and pressure a substance is found in the phase whose Gibbs free energy for each molecule is least. A gas is molecules far apart, each moving freely, whose pressure is the number of molecules in each unit of volume times the temperature as an energy, P = nkT, whatever the kind of molecule (Box 4.1). A real gas de-

parts from that because its molecules take room and attract one another by the dispersion force. The van der Waals equation, which carries both departures, gives a gas that becomes a liquid when squeezed below a critical temperature and passes smoothly into a dense fluid above it (Box 4.2). A liquid is molecules touching, ordered over a few neighbors and disordered beyond, flowing by passing over barriers, and paying a cost at its surface, the surface tension.

The phase diagram is a map of where each phase is found. Its lines are where two phases have equal Gibbs free energies, its triple point is where three meet, and its boiling curve ends at the critical point. Across a line of a first-order change a substance takes in a latent heat, the temperature times its jump in entropy. The slope of the line is the latent heat over the temperature times the change of volume (Box 4.3). A continuous change happens at a point because a symmetry separates the arrangements. Where neither a jump nor a symmetry separates them, the change is a crossover. Water's hydrogen bonds raise its boiling point far above that of its heavier neighbors. They hold ice in an open framework with more than twice the room of close packing, so ice floats and water's melting point falls under pressure (Box 4.4).

Between solid and liquid lie the glasses, liquids cooled too fast to find their rows, whose disordered arrangement is kept below a glass transition that shifts with the rate of cooling. Between them too lies soft matter. Polymers are chains that pull back by counting when stretched (Box 4.5). Liquid crystals are rods that share a direction while they flow. Colloids are small particles kept scattered in a liquid and jostled by Brownian motion. Gels are networks holding a liquid in their gaps. A plasma is a gas whose atoms have come apart into ions and free electrons. It cancels every charge beyond its Debye length and rings at its plasma frequency.

In every phase of this chapter but ice, the particles sit in no repeating pattern of places. Cooled further, most matter becomes a crystal, its atoms set in rows that repeat. Why do atoms repeat?

✶

KEY CONCEPTS

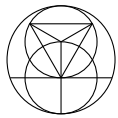
- **Phase.** A form of a substance that is the same throughout, with one arrangement of its molecules, meeting another phase of the same substance at a sharp boundary (the sense of this chapter, apart from the phase of a wave in The Ladder in Brief).
- **Ideal gas; ideal gas law.** A gas whose molecules are taken as points that exert no force on one another except in a collision; and its law, $PV = NkT$, or $P = nkT$ (Box 4.1).
- **Dispersion force.** The weak pull between any two atoms or molecules, arising because each one's momentary separation of charge induces a matching one in the other.
- **Van der Waals equation.** $(P + a/V_m^2)(V_m - b) = RT$, the ideal gas law with the room the molecules fill and their pull put in.
- **Critical point.** The temperature and pressure above which liquid and gas pass into each other with no jump; for water 647.096 kelvin and 22.064 million pascals (Box 4.2).
- **Supercritical fluid.** A substance above its critical point, whose density can be raised smoothly from a gas's to a liquid's with no boiling.
- **Critical opalescence.** The milkiness of a fluid near its critical point, from large fluctuations of its density.
- **Short-range order.** The arrangement of a molecule's nearest neighbors, held for a few molecular distances and lost over longer ones, as in a liquid.
- **Viscosity.** How hard a liquid must be pushed to make it flow at a given speed; it falls steeply as the liquid is warmed.

- **Surface tension.** The energy it takes to make one more unit of area of a liquid's surface, equal to the pull of the surface along each unit of length; 71.97 thousandths of a joule for each square meter for water at 25 degrees Celsius.
- **Phase diagram.** The map of the phases of a substance against temperature and pressure (Figure 4.1).
- **Sublimation.** The passing of a solid straight into a gas without melting.
- **Triple point.** The one temperature and pressure at which solid, liquid and gas are found together; for water 273.16 kelvin and 611.657 pascals.
- **Latent heat.** The heat a substance takes in to pass from one phase to another at a fixed temperature and pressure: $L = T\Delta S$.
- **First-order change; continuous change.** A change of phase with a jump in energy and entropy, and so a latent heat; and one in which the order grows from nothing at a point fixed by a symmetry that separates the ordered arrangement from the disordered one, with no latent heat.
- **Clausius-Clapeyron relation.** $dP/dT = L/(T\Delta v)$, the slope of a line of the phase diagram (Box 4.3).
- **Covalent bond.** A bond made by a pair of electrons shared between two atoms.
- **Lone pair.** A pair of an atom's outer electrons that takes no part in its bonds.
- **Hydrogen bond.** The attraction between a hydrogen atom bound to a strongly electron-pulling atom, such as oxygen, and a lone pair of another such atom; stronger than the dispersion force and weaker than a covalent bond.
- **Supercooled liquid.** A liquid held below its melting point without crystallizing.

- **Glass; amorphous solid; glass transition.** A solid whose molecules are caught in the disordered arrangement of a liquid; a solid with no repeat in its arrangement; and the temperature, depending on the rate of cooling, at which a cooling liquid stops flowing and becomes a glass.
- **Soft matter.** Matter whose structures are large against single molecules and held by weak forces, so that it yields to a gentle push and is reshaped by heat at ordinary temperatures.
- **Polymer; monomer.** A molecule made of many small molecules joined end to end into a chain; and each of those small molecules.
- **Liquid crystal; nematic.** A phase that flows as a liquid while its rod-like molecules share a direction; and the kind in which they share a direction and nothing else.
- **Colloid.** Small particles or droplets, between about a billionth and a millionth of a meter across, held scattered through another substance.
- **Brownian motion.** The ceaseless wandering of a small particle in a liquid or gas, struck unevenly by the molecules round it.
- **Gel.** A network of chains or particles reaching through a liquid and holding it in its gaps.
- **Plasma; ion.** A gas in which a large share of the atoms have lost electrons, a mixture of free electrons and ions; an ion being an atom or nucleus with a net charge.
- **Screening; Debye length.** The canceling of a charge's field at a distance by charges gathered round it; and the distance $\sqrt{(\varepsilon_0 kT/(ne^2))}$ beyond which a plasma cancels it.
- **Electric constant.** ε_0, the number that sets, in the international units, how strong a field a given charge makes.
- **Plasma frequency.** $\omega_p = \sqrt{(ne^2/(\varepsilon_0 m_e))}$, the frequency at which a plasma's electrons swing through its ions.
- **Amphiphile; micelle.** A molecule with one end drawn to water and the other shunning it, such as soap; and a ball of such molecules in water, tails inward and heads outward.

Part Two

Solids



Chapter 5

Crystals

CHAPTER OVERVIEW

A cool gathering of atoms settles in its arrangement of least energy, counting the energy of motion that quantum mechanics leaves in its ground state. Atoms of one kind are distinguished only by where they are, by the principle of identity: "what no comparison can distinguish, in any way at all, even in principle, is one thing and not two" (*The Quantum Passage*, Chapter 8, Section VI). And the laws are the same at every place. So the arrangement of surroundings that is least about one atom is, placed in the same way, least about every atom of its kind, and the least arrangement is one arrangement repeated: a crystal. Three cases fall outside the repeat, where the best surroundings cannot fit together or the atoms are given too little time. Helium stays liquid below about 25 bar because its zero-point energy outweighs packing, a liquid cooled fast is caught as a glass, and quasicrystals are ordered without repeating. X-rays show the repeat: a crystal sends them into strong beams only at the angles of Bragg's law (Box 5.1). The spots they make are the points of the crystal's reciprocal lattice, the lattice of the waves that the repeat fits exactly. A repeat can be turned onto itself only by a half, a third, a quarter or a sixth of a turn (Box 5.2), so crystals come in 14 kinds of lattice and 230 space groups. A space group is the whole set of moves that carry a crystal onto itself. The atoms vibrate about their places in 3N modes, independent ways of vibrating, whose longest waves are sound. Each mode holds energy in quanta, phonons, which are collective excitations of the

lattice, and any number of them can share a mode. A warm crystal takes up 3k of energy for each atom and each kelvin. As it cools its modes freeze out, and the energy it takes up for each kelvin falls as the cube of the temperature (Box 5.3). Its phonons also carry heat, best in diamond. A crystal slips by dislocations, lines along which its repeat is out of register, moving a row at a time, at a thousand to ten thousand times less stress, force on each unit of area, than sliding a whole plane needs (Box 5.4). Metals, whose bonds have no direction, bend, and covalent solids, whose bonds point, break. Ionic crystals cleave along planes that leave balanced charge on both faces, and molecular solids are soft. The chapter's reasoning gives the kinds of order a crystal can have and their counts, and measurement gives their sizes (Section VII).

I. Why Cool Atoms Repeat

Chapter 4 ended with a question: cooled further, most matter becomes a crystal, so why do atoms repeat?

Pour a little table salt onto a dark cloth and look at it through a magnifying glass. Every grain is a small cube, or a broken piece of one, with flat faces and square corners. The grains differ in size, and they all have the same shape. A lump of quartz from a hillside grows as six-sided columns with pointed ends, and every column of quartz, wherever it is found, has its faces at the same angles. Faces as flat as polished glass, at angles that never vary, are the outward sign of an inward order: the atoms inside are stacked in one arrangement, repeated over and over through the whole grain. A *crystal* is a solid whose atoms stand in one arrangement repeated through space.

So the reader's question is this: why do cool atoms arrange themselves in repeating patterns, and why do some solids bend while others break?

The first half of the answer rests on three things this book already has.

The first of the three things that the first half of the answer rests on is where a cool gathering of atoms settles. Chapter 2 showed that a system held at a fixed temperature and pressure settles where its Gibbs free energy, $G = E + PV - TS$, is least. When it is cold, the term TS, the temperature times the entropy (the logarithm of the number of the system's arrangements), is small, and the energy E rules. So at low temperature a gathering of atoms settles in the arrangement of least energy it can have: its ground state, the state with the least of what it can lose. That energy includes the energy of the atoms' motion that quantum mechanics leaves even in the ground state, the *zero-point energy*, which Chapter 3, Section VI, met in a vibrating bond. Matter crystallizes when it cools because the matter is settling toward its arrangement of least energy.

The second of the three things that the first half of the answer rests on is what tells one atom of a kind from another. Atoms of one kind are alike in every way that any measurement could register, apart from where they are and how they move. The likeness of atoms of one kind is the principle of identity at work, and *The Quantum Passage*, Chapter 8, Section VI, states the principle so: "The principle of identity says that what no comparison can distinguish, in any way at all, even in principle, is one thing and not two". A difference between two carbon atoms in themselves, a difference that no comparison could register, would be no difference. So two atoms of carbon in the same inner state, the same state of their nucleus and of their electrons, are two only by being at two places, and atoms of one kind are distinguished only by where they are.

The third of the three things that the first half of the answer rests on is that the laws are the same at every place. Whatever holds two atoms together at one place in a crystal holds them together in the same way at any other place, and the structure found at one place is the structure found at any other. That sameness of the laws from place to place is what keeps momentum, a body's mass times its velocity, unchanged when nothing acts on it (standard physics; Noether, 1918). In a crystal the sameness holds from one lattice place to the next, and Chapter 6 describes the momentum that this keeps for an electron in a crystal.

Now put the three together: the least energy, the principle of identity, and the sameness of the laws. Take one atom, and find the arrangement of neighbors round it that has the least energy. Take a second atom of the same kind, somewhere else. Nothing in the second atom differs from the first, by the principle of identity, and nothing in the laws at its place differs from the laws at the first, by the sameness of the laws. So whatever arrangement of surroundings is least about the first atom is, placed in the same way about the second, least about that atom too. The same holds for every atom of the kind. The bonds that hold atoms reach only to near neighbors, so the energy of the whole gathering is made up of the energies of its atoms with their surroundings. If every atom can have its least surroundings at once, no other arrangement gives any atom less, and that arrangement has the least energy of the whole. So the least arrangement gives every atom of a kind the same surroundings, and an arrangement in which every atom of a kind has the same surroundings as every other is one arrangement repeated. The least arrangement of a cool gathering of atoms is a crystal.

Where a crystal holds atoms of more than one kind, as salt holds sodium and chlorine, the argument runs for each kind at once. Every sodium atom has the same surroundings as every other, and so does every chlorine atom, and the whole is one group of a sodium and a chlorine repeated. The repeat needs names. The *lattice* of a crystal is the set of points, one for each copy of the repeated arrangement, from which the whole crystal is built by repeating. The smallest block whose copies, laid side by side, fill the crystal is its *unit cell*.

The argument says which arrangement is least, and a real crystal, grown at some temperature in some time, carries more than its least arrangement. A crystal has surfaces, where its atoms have fewer neighbors than inside, and it has flaws, places where an atom is missing or out of place. Atoms at a surface or at a flaw do have different surroundings from the atoms inside: atoms of a kind are alike in themselves, and they can still differ by their surroundings. Each surface and each flaw costs energy.

Each is found because a real crystal is grown at some temperature, in some time, with an edge, while the least arrangement has none of them. Section VI shows how much the flaws matter.

One more question completes the argument: do the best surroundings of each atom fit together? The argument shows that the least arrangement, if every atom can have its best surroundings at once, is a repeat. Three cases show where they cannot, or where the least arrangement is not reached, and each shows something.

The first case is helium. Helium-4 stays liquid down to the lowest temperature there is, unless it is squeezed above a pressure of about 25 bar, about twenty-five times the pressure of the air (Souris, Grucker, Dupont-Roc and Jacquier, 2010). A helium atom is light and its pull on its neighbors is the weakest of any atom's, and to hold it at one place in a lattice would confine it. Confinement costs energy of motion by the *uncertainty principle*. By that principle, the narrower the range of places in which a particle can be found, the wider the range of momenta it can be found to have (Volume One, Chapter 7, showed that confinement always costs energy in this way). For an atom held at a lattice place, that cost is its zero-point energy. For helium that cost is larger than the gain from packing the atoms in rows, so the least energy, counted with the zero-point energy, belongs to the liquid. Squeezed hard enough, the atoms are pushed close whatever they do, packing wins, and helium crystallizes.

The second case is glass. A liquid cooled faster than its molecules can move into rows is caught in its disordered arrangement, as Chapter 4, Section VII, showed. The least arrangement is a crystal, and the glass stays short of it for longer than any time that could be waited.

The third case is order without repeat. In some alloys, metals made of more than one element, the best local arrangement round an atom has a shape that cannot be repeated to fill space. There the atoms settle into an arrangement that is ordered throughout, with every atom's surroundings drawn from a few kinds, yet that never repeats. Such solids are quasicrystals, and Section III describes them.

So we now know why cool atoms repeat. The least arrangement gives every atom of a kind the same surroundings, because atoms of a kind differ only by where they are and the laws are the same everywhere. And the least arrangement is a crystal wherever those best surroundings fit together and the atoms are given time to reach them.

II. How We Know Crystals Repeat

Tilt a compact disc under a lamp and its surface shines with bands of color. The disc carries a track of tiny pits wound in rings about 1.6 millionths of a meter apart (the standard of the compact disc, IEC 60908). Light sent back from the rings adds up strongly only in directions where the waves from neighboring rings arrive in step. Those directions differ for each color, so the colors part. A regular pattern turns waves into strong beams in a few directions, and the directions tell the spacing of the pattern. The flat faces of a salt grain suggest that its atoms repeat. How can the repeat itself be seen, when the atoms are far too small for any microscope that uses light?

The answer is to use a wave as short as the spacing of the atoms. X-rays are light of very short wavelength, about a tenth of a nanometer, close to the distance between neighboring atoms in a solid. In 1912 Walter Friedrich, Paul Knipping and Max von Laue sent a narrow beam of X-rays through a crystal and recorded on a photographic plate a pattern of sharp spots (Friedrich, Knipping and Laue, 1912). The spots were the X-rays turned into strong beams in a few definite directions. The pattern of spots was the first sight of the repeat. A disordered solid or a liquid turns X-rays into a few blurred rings at most, and an arrangement ordered through the whole grain, as a repeat is, turns them into sharp spots (Section III describes the one kind of solid that does so without repeating). The scattering of a wave by a regular arrangement into strong beams in a few directions is *diffraction*. William Lawrence Bragg saw at once how to read the

spots (Bragg, 1912), and with his father, William Henry Bragg, he built the first X-ray spectrometer and used it to find the arrangement of the atoms in salt (Bragg and Bragg, 1913). Box 5.1 contains their reading.

Box 5.1. Bragg's law

Premises. (1) X-rays are waves of light of wavelength λ, read "lambda", comparable to the distances between atoms (standard physics). (2) In a crystal the atoms lie on families of flat, parallel, equally spaced planes, because the arrangement repeats; within one family the planes are a distance d apart (Section I). (3) Each plane sends back a small part of the X-rays falling on it as a faint mirror would, leaving at the same angle to the plane as they arrived (standard physics of waves). (4) Waves from different planes add to a strong beam only where they arrive in step, their paths differing by a whole number of wavelengths; elsewhere the waves of the many planes cancel (standard physics of waves). (5) The density of salt is 2.17 grams for each cubic centimeter (as tabulated for the mineral halite); the mass of one sodium and one chlorine atom together is 58.443 atomic mass units (standard atomic weights); and a cube of salt of side a, the side of its unit cell, holds four sodium atoms and four chlorine atoms (Bragg and Bragg, 1913). (6) The strongest X-ray line given out by copper, used in most laboratories, has the wavelength 0.15405929 nanometers (Deutsch et al., 2004).

Steps. X-rays falling at a glancing angle θ, read "theta", onto the planes of (2) are sent back at the same angle by every plane, by (3). The wave sent back by the second plane travels farther than the wave sent back by the first, by d sin θ on the way in and d sin θ on the way out (geometry), 2d sin θ in all. By (4), the beam is strong only where that difference is a whole number n of wavelengths: $n\lambda = 2d \sin \theta$. For salt, by (5), the cube of side a has a mass of 4×58.443 atomic mass units, so $a^3 = 4 \times 58.443/(2.17 \times N_A)$ cubic centimeters, with N_A the Avogadro constant, and $a = 0.563$ nanometers (computed). The planes parallel to the faces of the cube hold sodium and chlorine atoms alike and lie $a/2 = 0.282$ nanometers apart. By

(6), $\sin\theta = 0.15406/(2 \times 0.282) = 0.273$ for $n = 1$, so $\theta = 15.9$ degrees: the strong beam leaves 31.7 degrees from the direction of the beam that came in (computed).

Result. A crystal sends X-rays of wavelength λ into a strong beam from a family of planes of spacing d only at the glancing angles θ for which $n\lambda = 2d \sin\theta$, with n a whole number: *Bragg's law*. The angles of the strong beams give the spacings of the planes, and the strengths of the beams give where in the unit cell the atoms sit.

Run backward, Bragg's law measures. From the angles of the spots, the spacings of the planes follow, and from all the spacings, the shape and size of the unit cell. From the strengths of the spots, which depend on which atoms lie on which planes, follows the place of every atom in the cell. In salt the Braggs found each sodium atom surrounded by six chlorine atoms at the corners of an octahedron, a solid with eight triangular faces and six corners, and each chlorine by six sodiums. The arrangement in salt is the arrangement that I predicted in Volume One, Chapter 11, for ionic solids, each atom surrounded by as many atoms of the opposite charge as fit. X-ray diffraction has since found the arrangement of the atoms in crystals from salt to proteins with thousands of atoms in each unit cell.

The spots of a diffraction pattern have a second reading, and it is the one the next chapter needs. Every wave has a *wave vector*, an arrow that points along the wave's travel and whose length is 2π divided by its wavelength. A crystal turns an incoming X-ray into an outgoing one only where the outgoing wave vector less the incoming one equals one of a definite set of arrows that the crystal fixes. For each family of planes of spacing d, that set holds the arrows at right angles to the planes, with lengths $2\pi/d$ times a whole number. The whole set, for every family of planes, is itself a lattice, the *reciprocal lattice* of the crystal. Each spot of a diffraction pattern is one point of the reciprocal lattice, and the condition for a spot is Bragg's law written for wave vectors (mathematics). The reciprocal lattice is the lattice of the waves that the crystal's repeat fits exactly: a wave

whose wave vector is a point of the reciprocal lattice has the same value at every point of the crystal's lattice. Chapter 6 uses it as the home of the momentum an electron has in a crystal.

III. The Turns a Repeat Allows

Tile a bathroom floor with tiles of one shape and one size. Squares fill it, four meeting at each corner. Equilateral triangles fill it, six at each corner, and so do hexagons, three at each corner. Regular pentagons leave gaps: three of them at a corner leave a gap, and four overlap. Each corner of a regular pentagon is 108 degrees, and no whole number of 108-degree corners makes the 360 degrees round a point (mathematics). A floor tiled in squares looks the same after a quarter turn about the center of a tile, one tiled in triangles after a third of a turn, and one in hexagons after a sixth. Which turns can a repeated arrangement allow?

A turn that carries a crystal onto itself, so that after it every atom stands where an atom of the same kind stood before, must carry the crystal's lattice onto itself. Take two lattice points as close together as any two in the crystal, and turn the lattice by an angle about the first of them. The second goes to another point of the lattice. Turn the lattice by the same angle the other way about the second point, and the first goes to a lattice point too. Those two new points lie on a line parallel to the line joining the first two. The distance between them must be a whole number of the shortest distance between lattice points, or else there would be two lattice points closer together than the closest. For a turn by the angle θ, the distance between the new points is the shortest distance times $1 - 2\cos\theta$ (geometry), so $2\cos\theta$ must be a whole number. That holds only for turns by a half, a third, a quarter or a sixth of a turn, and for the whole turn. Box 5.2 shows the same result by a second route, from the numbers that describe the turn.

Box 5.2. The crystallographic restriction

Premises. (1) The points of a lattice are all the points $n_1a_1 + n_2a_2 + n_3a_3$, where a_1, a_2 and a_3 are three arrows from one lattice point to three neighboring ones, not all in one plane, and n_1, n_2 and n_3 are any whole numbers (Section I). (2) A turn that carries the lattice onto itself carries each of a_1, a_2 and a_3 to a lattice arrow, so the turn is written, in terms of the three arrows, as a table of three rows of three whole numbers (mathematics, from (1)). (3) The sum of the three numbers on the diagonal of such a table, its trace, is the same however the three arrows are chosen to describe the turn; for a turn by an angle θ about an axis, described with one arrow along the axis and two at right angles across it, the trace is $1 + 2 \cos \theta$ (mathematics).

Steps. By (2) the trace of the turn is a whole number, and by (3) it is $1 + 2 \cos \theta$; so $2 \cos \theta$ is a whole number. Since $\cos \theta$ lies between -1 and 1, $2 \cos \theta$ is one of -2, -1, 0, 1 and 2. So $\cos \theta$ is -1, $-1/2$, 0, $1/2$ or 1, and θ is 180, 120, 90, 60 or 360 degrees.

Result. A repeated arrangement can be turned onto itself by a half, a third, a quarter or a sixth of a turn, and by no other part of a turn: the *crystallographic restriction*. A turn by a fifth of a turn (72 degrees, for which $2 \cos \theta = 0.618$) or by a seventh or any smaller part is excluded for every crystal.

With so few turns allowed, crystals come in a fixed number of kinds. Combining the allowed turns with mirror reflections and with the shifts of the repeat, there are 14 kinds of lattice in three dimensions, which Auguste Bravais set out (Bravais, 1850). They are called the *Bravais lattices*. The count is a matter of sorting: each allowed set of turns and reflections fits only lattices of certain shapes. Bravais listed the shapes, with the ways of placing extra points at the centers of a cell's faces or of the cell itself that keep the same turns. The whole set of moves that carry a crystal onto itself, its shifts, turns, reflections and their combinations, is its *space group*. There are exactly 230 space groups, which Evgraf Fedorov and Arthur Schoenflies each counted in 1891, settling the list together in 1892 (Fe-

dorov, 1891; Schoenflies, 1891). Every crystal belongs to one of them. Salt has a cubic lattice, its unit cell a cube with atoms at the corners and at the centers of the faces. Iron at room temperature has a cubic lattice with an atom at the center of each cube, and ordinary ice has a hexagonal lattice, turned onto itself by a sixth of a turn.

The restriction holds for every repeat. In 1982 Dan Shechtman, cooling a melt of aluminum and manganese very fast, found a solid whose diffraction pattern had sharp spots, the sign of order reaching through the whole grain (Shechtman, Blech, Gratias and Cahn, 1984). The spots were arranged with the symmetry of a turn by a fifth or a tenth of a turn. By Box 5.2 no repeated arrangement can have that symmetry, so the solid's order reaches through the whole grain without repeating. Such a solid is a *quasicrystal*. Roger Penrose had already found two shapes of tile that cover a floor only without repeating (Penrose, 1974), with patterns of five-fold symmetry, and such tilings send waves into sharp spots arranged five-fold, as quasicrystals do. Quasicrystals that are stable, the arrangement of least energy for their mixture of atoms, were found from 1987 on, and one has been found in nature, in grains of a meteorite. Shechtman received the Nobel Prize in Chemistry in 2011 for the discovery. Quasicrystals show that order and repeat are two things. The argument of Section I gives a repeat where the best surroundings of each atom fit together into one block that can be repeated, and in a quasicrystal the best local arrangements fit together into an order that cannot be repeated. So sharp spots are the mark of order reaching through the whole grain, of which a repeat is one kind.

So we now know how the repeat is seen and what it allows. X-rays turned into sharp spots by Bragg's law reveal it, and the spots are the points of the reciprocal lattice. A repeat can turn onto itself only by a half, a third, a quarter or a sixth of a turn, which gives 14 kinds of lattice and 230 space groups.

IV. Vibrations in Steps

In a full stadium the crowd sends a wave round the stands. Each spectator stands up and sits down again in his own seat, a moment after his neighbor, and the wave runs round the whole stadium, though no spectator leaves his place. The atoms of a crystal can do the same. Each atom is held at its lattice place by its bonds to its neighbors, which act as springs, and if one atom is pushed, it pushes its neighbors, which push theirs. So the atoms can move about their places together, in waves that run along the crystal while every atom stays near its own place. How does a crystal hold such motion, and what does it carry?

A crystal of N atoms joined by springs has exactly 3N independent ways of vibrating, since each atom can move in three directions, and each way is a wave of one definite frequency running through the whole crystal (mathematics, for masses joined by springs). Such an independent way of vibrating is a *mode*. A wave shorter than twice the distance between neighboring atoms describes the same motion of the atoms as a longer one, because the atoms are only at the lattice places. So the modes run from the longest waves the crystal can hold down to waves of about twice the spacing.

The longest waves are sound. When the wave is long against the spacing, neighboring atoms move almost together, and the wave is an ordinary sound wave in the solid, running at the solid's speed of sound. The speed of sound in a solid is about 4,700 meters a second for copper, 5,100 for iron and 12,000 for diamond, against 343 in air at 20 degrees Celsius (as tabulated in the *CRC Handbook of Chemistry and Physics*). Three kinds of long wave run in each direction, one in which the atoms move back and forth along the wave's travel and two in which they move across it, and all three are sound. The waves of the lattice whose longest members are sound are called *acoustic* modes. Where the unit cell holds more than one atom, as salt's holds a sodium and a chlorine, there are also modes in

which the atoms of the cell move against one another, even in the longest waves. Modes in which the atoms of a cell move against one another are called *optical* modes, because in salt the sodium and the chlorine of a cell carry opposite charges and such a mode is set swinging by infrared light. Infrared light is light of longer wavelength than the red that the eye can see.

Each mode is a vibration of one frequency, f, and a vibration of one frequency holds energy only in whole quanta of hf, with h the Planck constant, as the springs of Chapter 2, Box 2.1, did. A bound wave must close on itself, so its energy levels are separate (Volume One, Chapter 7). And for a vibration whose pull back grows in proportion to the stretch, as a spring's does, the levels are equally spaced, hf apart (standard quantum mechanics of the oscillator). A quantum of vibration of a crystal's lattice, the energy hf added to one mode, is a *phonon*. *Measurement*, Chapter 3, Section IX, says what a phonon is: "a phonon is the smallest packet of vibration in a crystal, a quantum of the description of sound and not a separate thing in the crystal". A phonon is a *collective excitation*: a motion shared by many particles at once that comes in quanta. It is a quantum of the motion of the atoms of one crystal, and it exists only while the crystal does. So it stands apart from the particles of the kinds of Volume One, Chapter 1, the closed list of the electron, the quarks and the rest.

Are phonons excluded, as electrons are? Any number of phonons can share a mode, and the reason lies in what exclusion is about. Volume One, Chapter 1, Box 1.2, derives exclusion from the principle of identity for the particles of matter, whose spin is an odd number of halves, the *fermions*. Two such particles of one kind in one state could not be told apart and so would be one. So exchanging two of them multiplies their joint state by minus one, and a joint state of that kind with both particles in one state is zero, no state at all. A phonon is not a fermion. A mode holding two phonons is a vibration of the whole crystal holding the energy 2hf. A second phonon added to a mode that already holds one adds to the amount of vibration in that mode, as a second carrier of a force added to a filled state adds to the amount in it (the same box, premise 5). There is

nothing in such a mode to exchange but its quanta, and exchanging two of them gives back the same state unchanged, since a vibration holding two quanta is one and the same vibration whichever quantum is named first. So any number of phonons can share a mode, as any number of photons can share a state of light. Phonons therefore fill their modes in the way *bosons* fill their states, a boson being a particle whose spin is a whole number, of which any number of one kind can share a state. They fill so for the reason just given, the sameness of a vibration whichever quantum is named first, and not by being particles of the kinds. And since heat makes and unmakes phonons freely, their number is not kept, and, as for the photons of Chapter 2, Section XIII, their chemical potential is zero. So a mode of frequency f holds on average $1/(e^{hf/kT} - 1)$ phonons, by the Bose-Einstein form of Chapter 2, Box 2.5.

The shortest waves set a top to the frequencies. For copper the top frequency is about 7×10^{12} swings in each second, the frequency at which hf equals k times 343 kelvin (computed from copper's measured Debye temperature, the temperature that marks where a crystal's modes begin to freeze out, Section V). At room temperature, kT/h is 6.3×10^{12} swings in each second, nearly the same. So at room temperature nearly every mode of copper holds some phonons, and in a cold crystal only the long waves of low frequency do. In Section V I count the difference between the warm crystal and the cold crystal. So we now know how a crystal moves: its atoms vibrate about their places in 3N modes, the longest of which are sound. Each mode holds energy in quanta, the phonons, which are collective excitations of the lattice, and any number of them can share a mode.

V. Heat Taken Up and Heat Carried

A ticket machine at a station sells rides only for a whole fare. A traveler with less than a fare in his pocket rides nowhere, however close he comes, and a traveler with many fares can ride as often as he likes. The modes of

a crystal take energy as that machine sells rides: only in whole quanta of hf. How much energy does a crystal take up as it is warmed, and why does that change as it cools?

Heat capacity is the energy a system takes up for each rise of one unit in temperature, $C = dE/dT$ (Chapter 2, Section VII). It measures how much energy a solid takes up as it warms, not how much heat it holds. When a crystal is warm, kT is large against the quantum hf of every mode, and by equipartition (Chapter 2, Section X) each mode holds on average kT, half in its motion and half in its stretch. A crystal of N atoms has 3N modes, so it holds 3NkT, and it takes up 3Nk for each kelvin of rise. For a mole of atoms that is $3N_Ak = 3R = 24.94$ joules for each kelvin (computed). Pierre Dulong and Alexis Petit found this rule in measurements of many solid elements (Petit and Dulong, 1819), and it is the *Dulong-Petit law*. Measured at 25 degrees Celsius, a mole of copper takes up 24.47 joules for each kelvin, iron 25.09 and lead 26.40, close to the rule (as tabulated from the *CRC Handbook of Chemistry and Physics*).

Diamond takes up only 6.115 joules for each mole and each kelvin at 25 degrees, a quarter of the rule. Its carbon atoms are light and its bonds stiff, so its modes swing fast and their quanta are large: most of them hold a quantum hf larger than kT at room temperature. A mode whose quantum is far larger than kT holds almost no energy, since even one quantum is suppressed by its Boltzmann factor $e^{-hf/kT}$ (Chapter 2, Section X). That mode is frozen out, as the traveler without a full fare rides nowhere. So as any crystal cools, its modes freeze out one after another, from the highest frequencies down, and the energy it takes up for each kelvin falls away, toward none at the lowest temperature. Albert Einstein first explained the fall this way, with every atom swinging at one frequency (Einstein, 1907). Peter Debye counted it more exactly, from the fact that the modes of lowest frequency, which freeze out last, are the long waves of sound (Debye, 1912). Box 5.3 contains Debye's count.

Box 5.3. The heat capacity of a cold crystal goes as the cube of the temperature

Premises. (1) At low temperature only the long waves of sound hold energy; in a crystal of volume V, with a speed of sound v taken the same for the three kinds of sound wave, the number of modes with frequency below f is $3 \times (4\pi/3)f^3V/v^3$: the modes fill a ball in the three dimensions of the waves' directions and lengths, as the states of light did in Chapter 2, Box 2.6, and there are three kinds of sound in place of light's two senses of turning (standard physics of waves). (2) A mode of frequency f holds on average $hf/(e^{hf/kT} - 1)$ of energy (Section IV; Chapter 2, Box 2.5, with zero chemical potential). (3) The integral, the sum over a continuous range, of $x^3/(e^x - 1)$ from 0 to infinity is $\pi^4/15$ (mathematics). (4) The count of (1), carried up to the frequency f_D at which it reaches the crystal's whole number of modes, 3N, defines the *Debye temperature* Θ, read "theta", by $k\Theta = hf_D$; so $(4\pi/3)f_D{}^3V/v^3 = N$ (definition).

Steps. By (1), the modes with frequency between f and f + df number $12\pi f^2V\ df/v^3$. By (2), the energy they hold is $12\pi Vhf^3\ df/(v^3(e^{hf/kT} - 1))$; writing $x = hf/kT$ and using (3), the energy of all of them, at temperatures low enough that the top of the count is never reached, is $E = (12\pi V/v^3)(kT)^4/h^3 \times \pi^4/15$. By (4), $V/v^3 = 3Nh^3/(4\pi k^3\Theta^3)$, so $E = (3\pi^4/5)NkT^4/\Theta^3$. The heat capacity is $C = dE/dT = (12\pi^4/5)Nk(T/\Theta)^3$; for a mole of atoms, 1,944 joules for each kelvin times $(T/\Theta)^3$ (computed).

Result. When a crystal is cold, against its Debye temperature, the energy it takes up for each kelvin of rise falls as the cube of the temperature: the *Debye T^3 law*. The energy of its vibrations goes as T^4, three powers from the three dimensions of space and one from the energy each active mode holds, as for light in a box. For copper, whose Debye temperature is 343 kelvin (Kittel, 1996), the law gives 0.048 joules for each mole and each kelvin at 10 kelvin, against the 24.94 of the warm rule (computed).

The Debye temperature measures where a crystal's modes begin to freeze out: 343 kelvin for copper, 105 for lead, 2,230 for diamond (Kittel, 1996). A crystal well above its Debye temperature follows the Dulong-Petit law, and one well below follows the T^3 law. Diamond at room temperature, far below its 2,230 kelvin, is well on its way down. The heat that the crystal's modes take up is the part of a solid's heat capacity that the solid's lattice gives. In a metal the free electrons take up energy too, a part that falls in proportion to the temperature and outlasts the lattice's part at the lowest temperatures, and Chapter 6 adds it.

Phonons carry heat as well as hold it. A diamond feels cold to the touch, colder than glass at the same temperature, because it draws heat from a fingertip so fast. Jewelers tell a diamond from glass with a thermal tester, a warmed tip whose temperature drops fast when it touches a diamond, which measures exactly that. Where one end of a crystal is hotter than the other, the hot end holds more phonons. The phonons travel through the crystal at about the speed of sound, carrying their energy toward the cold end, until something scatters them. They are scattered by one another, since the bonds are not perfect springs and two waves in a crystal disturb each other. They are scattered too by flaws, by the crystal's boundaries, and by atoms of a different mass, which break the repeat for a vibration even where the chemistry is the same. The *thermal conductivity* of a solid, the heat it passes each second through each square meter of it for each kelvin of difference in temperature over each meter of length, is set by how fast and how far its phonons travel before they are scattered.

Diamond, with its fast sound and its large quanta, has few phonons at room temperature to scatter its heat-carrying waves. So it conducts heat better than any metal and almost any other solid at room temperature. It conducts about 2,100 watts for each meter and each kelvin for natural diamond at 25 degrees Celsius, and 3,150 for diamond made almost wholly of carbon-12, whose atoms of one mass scatter phonons less (Wei, Kuo, Thomas, Anthony and Banholzer, 1993). Copper conducts 401 (Kittel, 1996), though in a metal the free electrons carry most of the heat, more

than the phonons do (Chapter 6). Window glass conducts between 0.7 and 1.3 (Janssen and Warmoeskerken, 2006), a few hundred times less than copper, because its disorder scatters every short wave within a few atoms (Chapter 4, Section VII). So we now know how a crystal takes up heat and how it passes it on. Each of its 3N modes holds kT when warm and freezes out when kT falls below its quantum, which makes the energy it takes up for each kelvin fall as T^3 when cold. And its phonons carry heat until they are scattered.

VI. Why Some Solids Bend and Others Break

Drop a stick of chalk and it snaps. Bend a copper wire and it bends, and stays bent. Set a knife edge on a clear crystal of rock salt and tap it, and the crystal splits along a flat face, as clean as a cut. Press a candle with a thumbnail and the wax dents. All four are crystals, or are made of crystals, and all four repeat, yet they answer a push in four different ways. Why?

The answer lies in what holds the atoms of each, and Volume One, Chapter 11, describes four kinds of bond. In a *covalent* solid, such as diamond or silicon, the atoms are joined by covalent bonds, each a pair of electrons shared between two atoms, and the bonds point in fixed directions. Each carbon atom of diamond is bonded to four neighbors at the corners of a tetrahedron. In a *metal*, each atom gives its few loosely held outer electrons to be shared with all its neighbors at once, so the shared electrons move through the whole piece of metal and the bond between the atoms has no direction. A bond made by outer electrons shared among all the atoms of a metal is the *metallic bond*. In an *ionic* solid, such as salt, each atom of one kind gives up an electron to an atom of another, and the two, now ions of opposite charge, are held by the electric pull between them. Each is surrounded by as many of the opposite charge as

fit: six, in salt (Section II). And in a *molecular* solid, such as wax or ice, whole molecules are held to one another only by the dispersion force or by hydrogen bonds (Chapter 4).

Each kind of bond answers a push in its own way. In a covalent solid every atom is fixed in its directions, and moving one plane of atoms past the next means breaking bonds. Such solids are hard, and they break rather than bend. In a metal the bond has no direction, and a plane can slide past its neighbor, a row at a time, with every atom keeping its share of the bond. Metals bend, and they can be hammered flat and drawn out into wire. In an ionic solid a slide of one plane past the next by half a spacing brings like charges face to face, which costs a great deal of energy, so such solids resist sliding. They are hard, and they split cleanly. And molecular solids, whose molecules are held to one another weakly, are soft and melt at low temperatures. Three questions complete the account. Why does sliding need a row at a time, why does a covalent solid break where a metal bends, and why does an ionic solid split cleanly?

The first question starts from the stiffness of a solid against sliding. Push the top face of a block sideways while the bottom face is held, and the block leans. The force on each unit of area of the face, divided by the amount of lean, is the solid's *shear modulus*, written G, its stiffness against sliding one layer over the next. To slide the upper half of a perfect crystal over the lower half along a plane, all at once, every bond across that plane must be strained at the same moment to the point where it gives way. Yakov Frenkel estimated the stress, the force on each unit of area, that this needs: about $G/2\pi$, of order a tenth of the stiffness (Frenkel, 1926). Real metals slip at stresses a thousand to ten thousand times smaller. In 1934 Geoffrey Taylor, Egon Orowan and Michael Polanyi each gave the reason (Taylor, 1934; Orowan, 1934; Polanyi, 1934): a crystal slides a row at a time, never a whole plane at once.

Think of a large heavy carpet that has to be moved a hand's breadth across a floor. Dragged by one edge, it will not budge, because the whole of it rubs on the floor at once. Push a ruck into it at one edge and then push the ruck along, and the ruck runs across the carpet with little effort.

When it reaches the far side, the whole carpet has moved over by the width of the ruck. A crystal slides the same way, by a *dislocation*: a line in the crystal along which the repeat is out of register, the edge of an extra half-plane of atoms pushed in between two planes of the crystal. Box 5.4 describes a dislocation crossing a crystal.

Box 5.4. A dislocation moves a row at a time

Premises. (1) To slide the upper half of a perfect crystal over the lower half by one spacing of the atoms, all at once, every bond across the plane of sliding must be strained to its breaking point at the same moment; the stress this needs is about $G/2\pi$ (Frenkel, 1926). (2) In a crystal with a dislocation, an extra half-plane of atoms ends at a line inside the crystal; away from that line the atoms on the two sides of the plane of sliding are bonded across it as in a perfect crystal, and only along the line are the bonds across it out of their usual register (standard physics of dislocations; Taylor, 1934). (3) Moving the dislocation by one spacing needs only the atoms of one row along the line to change partners across the plane of sliding: the bonds of that row are remade with the next half-plane over, and the line moves one spacing on (the same). (4) Near the line, atoms on one side are pushed one way and atoms on the other side the other way; as the line moves, the energy given up on one side of it is nearly the energy taken up on the other, so the barrier to moving it by one spacing is small, smallest where the bonds have no direction (standard physics of dislocations).

Steps. By (3), each step of the line across the crystal remakes the bonds of one row only, while the rest of the plane of sliding stays as it was. When the line has crossed the whole plane and left the crystal at the far side, every row has changed partners once, and the upper half of the crystal has moved over the lower half by one spacing: the same slip that (1) makes all at once. At every moment of the crossing only the bonds along one line are changing, so the stress needed is only what pushes one row over the small barrier of (4), not what (1) needs to break a whole plane.

Result. A crystal slips by dislocations moving a row at a time, and the stress needed is far below the stress for sliding a whole plane at once: a thousand to ten thousand times lower in metals (Taylor, 1934; Orowan, 1934; Polanyi, 1934). The slip a dislocation makes when it crosses the crystal is one spacing of the atoms; a bent wire has been slipped by very many dislocations crossing it.

The second question, why a covalent solid breaks where a metal bends, is now answered by what the barrier of a row depends on. In a metal the shared electrons hold an atom equally to whichever neighbors it has, so the atoms of a row change partners with no bond that points one way to break. The barrier is small, dislocations move at low stress, and the metal bends. In a covalent solid every step of a dislocation breaks bonds that point in fixed directions and makes new ones, row by row. The barrier is high, and at room temperature its dislocations hardly move. So when a covalent solid is pushed, the stress in it rises without any slip to relieve it, until it reaches the stress at which the bonds across one plane part and a crack opens. Parting the solid breaks bonds along one plane, once, while sliding it would break and remake bonds at every row the dislocation crossed. The crack comes first, and the solid breaks: chalk snaps, glass and diamond shatter, and a silicon wafer cracks before it bends.

The third question, why an ionic solid splits cleanly, is answered by the charges on the faces. A plane parallel to a face of salt's cubic cell holds sodium and chlorine ions alike, in a checkerboard, as many of each as of the other. Parting the crystal along such a plane leaves each new face with as much positive as negative charge, balanced, and the two halves come apart without being held by any net charge. A plane cut across the corners of the cube holds ions of one kind only, all sodium or all chlorine, the planes taking turns. Parting along it would leave one face all positive and the other all negative, and the pull between them would hold the crystal together with far more energy. So salt parts along its cube faces, in each of the three directions of the cube, and splits into smaller cubes and flat-

faced blocks. The parting of a crystal along a flat plane of its lattice is *cleavage*, and ionic crystals cleave along the planes that leave balanced charge on both faces.

Real solids are seldom perfect single crystals: they hold flaws, and most are made of many crystals. A *vacancy* is a lattice place with its atom missing, and an *interstitial* is an extra atom squeezed into a gap between lattice places. Each costs energy, and at a given temperature a crystal holds a share of them set by their Boltzmann factor (Chapter 2, Section X), more as it is warmed. Atoms of the solid's own kind move through it by stepping into vacancies. The dopants of a silicon chip, atoms of another element added on purpose in small amounts (Chapter 7), move partly by vacancies and partly by silicon atoms knocked out of their places. An atom as small as the carbon in a steel moves another way, stepping from gap to gap between the places of the iron lattice. Most metals and rocks are made of many small crystals, called *grains*, each a crystal of its own with its lattice turned a different way from its neighbors'. The surface where two grains meet is a *grain boundary*. A dislocation that reaches a grain boundary is stopped there, because the lattice beyond is turned another way. So the finer the grains, the more boundaries block the dislocations and the stronger the metal (Hall, 1951; Petch, 1953). And dislocations block one another. Bend a paper clip back and forth and it grows stiffer, because its dislocations multiply and tangle until each can hardly move. The paper clip's stiffening is *work hardening*, and bent a little more, the stiffened wire breaks.

So we now know why some solids bend and others break. A crystal slips by dislocations moving a row at a time, which needs a thousand to ten thousand times less stress than sliding a whole plane. In a metal the bond has no direction and dislocations move easily, so it bends. In a covalent solid each row's move breaks bonds that point, so the stress opens a crack first and it breaks. And an ionic crystal parts along the planes that leave balanced charge on both faces.

VII. Counts and Measured Values

The Preface asked three questions of every level, and it answered one of them, which wholes last, with a split: the rule comes from structure, and the values come from measurement. Crystals show the same split clearly. Which of this chapter's findings come from the reasoning alone, and which must be measured?

The reasoning alone gives counts: how many arrangements fit, and how many ways there are. The least arrangement of atoms that fit together is a repeat. A repeat can be turned onto itself by a half, a third, a quarter or a sixth of a turn and by no other part of a turn. There are 14 kinds of lattice and 230 space groups. A crystal of N atoms has 3N modes of vibration, and any number of phonons can share a mode. A warm crystal takes up three times k of energy for each atom and each kelvin, the number three counting the three directions in which each atom can move. A cold crystal's heat capacity falls as the cube of the temperature because space has three dimensions. Chapter 6 adds one more count, two electrons for each band and each unit cell. Each of these is a whole number of possibilities, or a power fixed by such a number, and none is a length, an energy or a temperature.

The sizes come from measurement. The spacing of salt's lattice, 0.563 nanometers, comes from the measured density of salt and the mass of its atoms (Box 5.1), and the X-rays measure it. Which lattice each substance takes, cubic for salt, cubic with a center atom for iron, hexagonal for ice, is found by X-rays and by computing which arrangement has the least energy for those atoms. The speeds of sound, the Debye temperatures, the thermal conductivities and the stresses at which metals slip are set by the masses of the atoms and the strengths of their bonds, and in this book each of them is taken from measurement. So the structure says what kinds of order there can be, and the atoms and their bonds, as measured, say which one each substance takes and how large it is.

In Use

Steel is iron made strong by its flaws. Pure iron at room temperature is a crystal with a cubic lattice and an atom at the center of each cube, and it is soft, because its dislocations move easily. Steel is iron with between 0.02 and 2.14 percent of carbon by weight (as given in the standard definition of plain carbon steel). The small carbon atoms sit in the gaps between the iron atoms, as interstitials, and the strain round each one holds back the dislocations that pass, so the steel is harder and stronger. Heated, iron changes its lattice to a cubic one with atoms at the centers of the faces, which takes more carbon into its gaps. Quenched, cooled suddenly in water or oil, it has no time to give the carbon back, and its lattice is trapped in a strained form called martensite, hard but brittle, because its dislocations can hardly move. An *alloy*, a metal made of more than one element, is strengthened by the same means. Atoms of another size pin the dislocations, fine grains block them with their boundaries, and, in a wire drawn cold, work hardening tangles them. Stainless steel holds at least 10.5 percent of chromium (European standard EN 10088-1), which forms a thin film of chromium oxide on the surface that keeps the iron beneath from rusting (standard accounts of stainless steel).

X-ray crystallography, the finding of the arrangement of atoms from Bragg's law, found the shape of the molecule that carries heredity. Each molecule of DNA, deoxyribonucleic acid, repeats along its length, though DNA forms no crystals in three dimensions. In 1953 Rosalind Franklin and Raymond Gosling published an X-ray photograph of wet fibers of DNA whose cross-shaped pattern of spots showed a helix (Franklin and Gosling, 1953). The same issue of *Nature* carried James Watson and Francis Crick's structure for DNA, two chains wound round each other with their bases paired between them, which drew on that pattern (Watson and Crick, 1953). Since then X-ray diffraction has found the arrangement of the atoms in a great many of the proteins and other large molecules of

life. Of the 254,149 structures held in the Protein Data Bank on 21 May 2026, about 80 percent were found by X-ray diffraction (Protein Data Bank, as reported for that date). Medicines are designed to fit the shapes it finds, a method called structure-based drug design (standard accounts of the method).

A quartz watch keeps time with a crystal. Quartz has no center of symmetry in its space group: no point about which every atom has a twin at the same distance on the opposite side. So squeezing a quartz crystal shifts its positive and negative charges unequally and a voltage appears across it, and a voltage across it makes it flex. A voltage from a squeeze, and a flex from a voltage, make up the *piezoelectric effect*. Jacques and Pierre Curie discovered the piezoelectric effect (Curie and Curie, 1880). A small piece of quartz cut in the shape of a tuning fork, driven by a voltage in time with its own swing, rings at a frequency set by its size, its stiffness and its density. The crystals of watches are cut to ring 32,768 times a second, which is 2^{15} (the standard frequency of the crystals of watches and clocks), and a circuit halves that frequency fifteen times over to give one tick each second. Walter Cady built the first oscillator held in time by a quartz crystal in 1921 (Cady, 1922). The quartz keeps time well because its vibration loses very little energy at each swing: the energy it stores, times 2π, is 10^4 to 10^6 times the energy it loses in each swing (standard accounts of crystal oscillators). Quartz crystals keep the time in watches, clocks, radios, computers and telephones (the same accounts).

Summary

A cool gathering of atoms settles in its arrangement of least energy, counting the zero-point energy, because its Gibbs free energy is then ruled by its energy. Atoms of one kind are distinguished only by where they are, by the principle of identity, and the laws are the same at every place. So the arrangement of surroundings that is least about one atom is least about every atom of its kind. The least arrangement is one arrangement re-

peated, a crystal, wherever those best surroundings fit together and the atoms have time to reach them. Helium stays liquid to the lowest temperature below about 25 bar because its zero-point energy outweighs the gain of packing. A liquid cooled too fast is caught as a glass, and quasicrystals are ordered without a repeat. X-ray diffraction sees the repeat: a crystal sends X-rays into strong beams at the angles of Bragg's law, $n\lambda = 2d \sin \theta$ (Box 5.1). The spots of a diffraction pattern are the points of the reciprocal lattice. A repeat can be turned onto itself by a half, a third, a quarter or a sixth of a turn and by no other part (Box 5.2), so there are 14 kinds of lattice and 230 space groups.

The atoms of a crystal vibrate about their places in 3N modes, the longest of which are sound. Each mode holds energy in quanta, the phonons, which are collective excitations of the lattice, apart from the kinds of particle, and any number of them can share a mode. Heat capacity is the energy taken up for each rise of one unit in temperature. It is 3k for each atom when warm, the Dulong-Petit law, and it falls away as the modes freeze out when cold, as the cube of the temperature (Box 5.3). Phonons also carry heat, until they are scattered, and diamond, with its fast sound and large quanta, carries it best. A crystal slips by dislocations moving a row at a time, which needs a thousand to ten thousand times less stress than sliding a whole plane (Box 5.4). In a metal the bond has no direction and dislocations move easily, so metals bend. In a covalent solid each row's move breaks bonds that point, so the stress opens a crack first and the solid breaks. An ionic crystal parts along planes that leave balanced charge on both faces, and molecular solids are soft. The reasoning gives the kinds of order and their counts, and the atoms and their bonds, as measured, give the sizes (Section VII).

The atoms of a crystal repeat, and so does everything that acts on an electron among them. In a repeating array the electrons reach through the whole crystal. What states can they take?

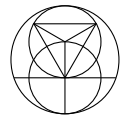
✶

KEY CONCEPTS

- **Crystal.** A solid whose atoms stand in one arrangement repeated through space.
- **Principle of identity.** What no comparison can distinguish, in any way at all, even in principle, is one thing and not two (*The Quantum Passage*, Chapter 8, Section VI).
- **Zero-point energy.** The energy of motion that a confined particle keeps even in its ground state; for helium it outweighs the gain of packing, so helium stays liquid below about 25 bar.
- **Lattice; unit cell.** The set of points, one for each copy of the repeated arrangement, from which a crystal is built; and the smallest block whose copies fill the crystal.
- **Diffraction.** The scattering of a wave by a regular arrangement into strong beams in a few directions.
- **Bragg's law.** $n\lambda = 2d \sin\theta$: X-rays of wavelength λ leave planes of spacing d in a strong beam only at those glancing angles θ.
- **Wave vector; reciprocal lattice.** An arrow along a wave's travel whose length is 2π over its wavelength; and the lattice of wave vectors whose waves the crystal's repeat fits exactly, whose points are the spots of a diffraction pattern.
- **Crystallographic restriction.** A repeat can be turned onto itself by a half, a third, a quarter or a sixth of a turn and by no other part of a turn (Box 5.2).
- **Bravais lattices; space group.** The 14 kinds of lattice in three dimensions; and the whole set of moves that carry a crystal onto itself, of which there are 230.

- **Quasicrystal.** A solid ordered throughout, with sharp diffraction spots, that never repeats, such as one with five-fold symmetry.
- **Octahedron.** A solid with eight triangular faces and six corners.
- **Mode.** One of the 3N independent ways a crystal of N atoms can vibrate, each a wave of one frequency.
- **Acoustic and optical modes.** The modes whose longest waves are sound; and, where a unit cell holds more than one atom, the modes in which its atoms move against one another.
- **Phonon; collective excitation.** A quantum of vibration of a crystal's lattice; and a motion shared by many particles at once that comes in quanta. Any number of phonons can share a mode, and they stand apart from the kinds of particle.
- **Heat capacity.** The energy taken up for each rise of one unit in temperature, $C = dE/dT$.
- **Dulong-Petit law.** A warm crystal takes up 3k for each atom and each kelvin, 24.94 joules for each mole and each kelvin.
- **Debye temperature; Debye T^3 law.** The temperature Θ at which $k\Theta$ equals the quantum of a crystal's highest mode; and the fall of a cold crystal's heat capacity as $(T/\Theta)^3$ (Box 5.3).
- **Thermal conductivity.** The heat a solid passes each second through each square meter for each kelvin of difference over each meter of length.
- **Covalent, metallic, ionic and molecular solids.** Solids held by shared pairs of electrons in fixed directions; by outer electrons shared among all the atoms, a bond with no direction; by the pull between ions of opposite charge; and by the weak pulls between whole molecules.
- **Shear modulus.** A solid's stiffness against sliding one layer over the next.
- **Dislocation.** A line in a crystal along which the repeat is out of register, the edge of an extra half-plane of atoms; it moves a row at a time and lets the crystal slip at low stress (Box 5.4).

- **Cleavage.** The parting of a crystal along a flat plane of its lattice; ionic crystals cleave where both new faces carry balanced charge.
- **Vacancy; interstitial.** A lattice place with its atom missing; and an extra atom in a gap between lattice places.
- **Grain; grain boundary.** One of the many small crystals of a metal or rock; and the surface where two grains, their lattices turned differently, meet.
- **Work hardening.** The stiffening of a metal as it is bent, from its dislocations multiplying and tangling.
- **Alloy.** A metal made of more than one element.
- **Piezoelectric effect.** The voltage that appears across a crystal with no center of symmetry when it is squeezed, and the flexing a voltage gives it.



Chapter 6

Bands

CHAPTER OVERVIEW

Copper conducts more than 10^{25} times better than fused quartz, and the reason lies in the states an electron can take in a repeating crystal. A shift by one step of the lattice leaves the crystal unchanged. So the states of an electron of definite energy can be chosen so that each, shifted by one step, is the same state turned forward by a phase, the stage of a wave's swing, by the same amount at every step: Bloch's theorem (Box 6.1). Such a state belongs to the whole crystal and is labeled by its crystal momentum, the part that momentum plays in a crystal, within the Brillouin zone, a single cell of the lattice of the waves the crystal fits. Each state of the single atom becomes a band of such states, wider the more neighboring atoms' waves overlap. Between bands lie gaps with no state wherever no band reaches across, and bands may also overlap. Each band holds two electrons, of opposite spin, for each cell of the repeat (Box 6.2). The electrons fill the bands from the bottom up to the Fermi level, the top of the filling, which in copper lies 7.03 eV above the bottom of its band (Box 6.3). Where the filling stops inside a band, the smallest push moves electrons and the solid is a metal. Where it stops at the top of a band with a gap above, a small push moves none, and the solid is an insulator. An odd count of electrons in each cell leaves a band partly filled, except where the electrons' push on one another holds each at its own atom, which makes a Mott insulator. An even count gives an insulator where a gap lies above the last full band and a metal where the bands overlap (Figure 6.1). Only the electrons

within kT of the Fermi level take up heat, so the electrons' heat capacity is small and in proportion to the temperature. In a semiconductor the gap is small, and heat lifts a few electrons across. Both they and the empty states they leave, the holes, carry current, more as the solid warms. The holes move as positive charges and show it in the Hall effect, a voltage across a strip carrying a current in a magnet. A perfect, motionless crystal lets its electrons pass unhindered. Resistance comes from vibrations, flaws and collisions of electrons in which the crystal takes up momentum, and all but the flaws vanish at the lowest temperature. A solid takes up only photons that can lift an electron to an empty state. The gap sets a semiconductor's color (Table 6.1), a metal sends back light below its plasma frequency and passes it above, and copper and gold take their colors from bands lying deeper than the one their outer electrons fill.

I. Copper, Glass and Silicon

Chapter 5 ended with a question: in a repeating array the electrons reach through the whole crystal, so what states can they take?

Look at a lamp cord cut open. Inside the plastic sleeve is a bundle of fine copper wires, and the current that lights the lamp runs through the copper and not through the plastic. Look at the window beside the lamp: its glass lets the light through and holds back the current entirely. And inside the switch on the wall, or the dimmer, or any of the small black packages of a computer, is a third kind of solid, silicon. It passes a little current, more when it is warm, and it can be made to pass a great deal by adding a trace of another element to it. All three are solids made of atoms with electrons, and every atom of each holds its electrons by the same electric pull.

The differences between them are among the largest differences that physics measures. An electric *current* is charge in motion, as Chapter 3 met it, counted as the charge that passes a point each second, in amperes. A *voltage* between two points is the energy that each unit of charge gains or

gives up in passing from one point to the other, in volts, one volt being one joule for each coulomb, the unit of charge (Chapter 3, Box 3.3). For most solids, the current through a piece is in proportion to the voltage across it, and the ratio of the voltage to the current is the piece's *resistance*, measured in ohms. This proportion is *Ohm's law*, which Georg Ohm found in 1827 (Ohm, 1827). The resistance of a piece depends on its shape as well as on its material: a long thin wire resists more than a short thick one. The material's own part is its *resistivity*, the resistance of a cube of it one meter on a side, measured between two opposite faces, in ohm meters.

At 20 degrees Celsius the resistivity of copper is 1.678×10^{-8} ohm meters, and that of pure silicon is about 2.3×10^{3}. That of window glass lies between 10^{11} and 10^{15}, and that of fused quartz, glass made of pure silica, is 7.5×10^{17} (standard tables of resistivity). Fused quartz resists the passing of charge more than 10^{25} times more than copper does, though both are made of atoms held by the same force. And as copper warms, its resistance rises, while the resistance of silicon falls, steeply.

So the reader's question is this: why do metals conduct, insulators not, and semiconductors a little?

The first answer was given in 1900, three years after Joseph John Thomson found the electron (Thomson, 1897). Paul Drude pictured a metal as a box of fixed positive ions with a gas of free electrons moving among them, bumping into the ions as the molecules of a gas bump into one another (Drude, 1900). A voltage pushes the electrons along between bumps, and the bumps stop each one from gathering more and more speed. So the electrons drift along at a steady speed in proportion to the push, and that is Ohm's law. The picture works, and it is the start of every later account. It is called the *free-electron model*. It also leaves three questions open, which we answer in this chapter.

The first of the three open questions is why the electrons go so far between bumps. In a crystal of copper the ions stand a quarter of a nanometer apart, yet Section VIII finds that an electron in copper at room tem-

perature travels about 40 nanometers, past some hundred and fifty ions, before anything turns it aside. The second open question is why the electrons of a metal take up almost no heat. A gas of free particles takes up three halves of k of energy for each particle and each kelvin (Chapter 2, Section X), and copper has one free electron for each atom. So copper should take up half as much again as the 3k for each atom that its lattice takes (Chapter 5, Section V). Measured, it takes up 24.47 joules for each mole and each kelvin at 25 degrees Celsius, close to the lattice's 24.94 alone. The third open question is the one this chapter is named for: why glass has no free electrons at all, and why silicon has a few.

All three answers come from the same place: the states an electron can take in a repeating crystal. Chapter 2 has given the way fermions fill their states: one to a state, from the lowest up to a top. A *fermion* is a particle whose spin is an odd number of halves, such as the electron, whose spin is one half. Chapter 5 has given the repeat of the crystal. What remains is to find the states the repeat allows.

II. A Wave in a Repeating Crystal

Picture a long cloister with a row of identical alcoves, and a choir with one singer standing in each alcove. Every singer sings the same song, at the same pitch and the same loudness, but each starts a fixed fraction of a beat after the singer to the left. Walk along the cloister and every alcove is the same, and so is the song in it. The one thing that changes from one alcove to the next is how far along in the beat its singer is, and it changes by the same amount at every alcove. The fraction can be anything from nothing at all, when the whole choir sings in unison, up to a whole beat, and a whole beat behind is the same as in unison again. What do the states of an electron look like in a crystal, where every cell of the repeat is like every other?

The electron is found as a wave, as Volume One, Chapter 7, found for the electron of the hydrogen atom, and in a crystal its wave runs among very many atoms. The crystal repeats: Chapter 5, Section I, found that its atoms stand in one arrangement repeated through space. So the pull on an electron at any point is the same as the pull at the same point of every other cell. Shift the whole crystal by one step of its lattice, from one lattice point to the next, and it is unchanged: every atom stands where an atom of the same kind stood before, and the laws are the same at every place.

Now take a state of the electron with a definite energy, and shift it by one step of the lattice. Since the crystal and its laws are unchanged by the shift, the shifted state is again a state of the same energy in the same crystal. What can differ between the state and its shifted copy? Only something that no finding registers, since every cell of the crystal is like the next. The *phase* of a wave is the stage of its swing at a place, counted as a fraction of a whole turn of the swing, as The Ladder in Brief gave it. The stage of a wave's swing is the wave sense of the word phase, apart from the phases of matter of Chapter 4. A wave multiplied everywhere by one fixed phase factor, which turns the wave's swing forward by a fixed fraction of a turn, is found the same in every measurement. Volume One, Chapter 7, Section IV, met such a factor as one "that changes no finding". So the states of definite energy can be chosen so that each, shifted by one step of the lattice, is the same state turned forward by a phase, and by the same phase at every step. The choir's song is so: the same in every alcove, and moving on by the same fraction of a beat from each to the next. Box 6.1 carries the argument through, and its result, named *Bloch's theorem*, is the one just stated.

Box 6.1. Bloch's theorem in words

Premises. (1) A crystal repeats: shifting it by any arrow a from one lattice point to another leaves every atom where an atom of the same kind stood, so the pull on an electron is the same at r and at r + a, for every point r (Chapter 5, Section I). (2) A shift that leaves the crystal and its laws unchanged carries a state of definite energy into a state of the same energy;

and two such shifts, made one after the other in either order, give the same result (standard quantum mechanics). (3) A wave multiplied everywhere by one fixed phase, a factor $e^{i\theta}$ that turns its swing forward by the angle θ, read "theta", is found the same in every measurement (Volume One, Chapter 7, Section IV; standard quantum mechanics). (4) A shift keeps the total weight of the possibilities: the change it makes is unitary (Chapter 2, Section I), so a factor it multiplies a state by has size one. (5) For counting, a crystal of N cells is taken closed on itself, so that N steps of the lattice along each direction bring an electron back to where it began; the count found this way holds for any large crystal, whatever its surfaces (standard physics; Born and von Kármán, 1912).

Steps. By (2), the shifts and the energy can be found together, so the states of one energy can be chosen so that every shift carries each of them into itself multiplied by a number (mathematics). By (4), that number has size one, so it is a phase, $e^{i\theta(a)}$, by (3) a factor that changes no finding. A shift by a and then by b is a shift by $a + b$, so the phases add: $\theta(a + b) = \theta(a) + \theta(b)$; the angle is then in proportion to the shift, $\theta(a) = k \cdot a$, with k a wave vector, the same at every step of the lattice (mathematics). Two wave vectors that differ by a point of the reciprocal lattice give the same phase at every lattice arrow, since a wave whose wave vector is a point of the reciprocal lattice has the same value at every point of the crystal's lattice (Chapter 5, Section II); so every state is labeled by one k within a single cell of the reciprocal lattice centered on zero, the *Brillouin zone*. Along a row of lattice points a distance a apart, k runs from $-\pi/a$ to $+\pi/a$, and the phase from one point to the next, ka, runs over one whole turn. By (5), the phase over N steps must come back to the start, $e^{ikNa} = 1$, so k takes N values in the zone, spaced $2\pi/(Na)$ apart: one for each cell of the crystal.

Result. In a crystal, the states of an electron of definite energy can be chosen so that each, shifted by one step of the lattice, is the same state turned forward by a phase that is the same at every step: $\psi(r + a) = e^{ik \cdot a}\psi(r)$, with ψ, read "psi", the electron's wave. The rule of the same phase at every step of the lattice is *Bloch's theorem* (Bloch, 1928). Each state is labeled by its wave vector k in the Brillouin zone, and for each kind of state there are exactly as many values of k as the crystal has cells.

A state of this kind is a *Bloch state*, after Felix Bloch, who found the result for electrons in crystals in 1928. The theorem answers Chapter 5's question, what states the electrons of a crystal can take, at once. Since a phase changes no finding, the electron in a Bloch state is found with the same weight in every cell of the crystal: it belongs to the whole crystal alike, and to no one atom. The electrons of a crystal reach through the whole of it because the crystal repeats.

The label k plays the part that momentum plays for a free particle. For a free electron, a state of definite momentum p is a wave whose wave vector is $p/\hbar$. Here $\hbar$, read "h-bar", is the *reduced Planck constant*: Planck's constant h divided by 2π, $1.054571817... \times 10^{-34}$ joule seconds. In a crystal the product $\hbar k$ is called the electron's *crystal momentum*. It differs from momentum in one way that matters later in this chapter. Two wave vectors that differ by a point of the reciprocal lattice label the same state, so every k can be placed in one cell of the reciprocal lattice, centered on zero, called the *Brillouin zone* (Box 6.1). So crystal momentum is kept in every change only up to a point of the reciprocal lattice: the crystal as a whole can take up such a step of momentum. It does so when it turns an X-ray into one of the strong beams of Bragg's law (Chapter 5, Section II). Section VIII finds that this is where some of a metal's resistance comes from.

So we now know what states an electron can take in a crystal. They are the same in every cell up to a phase, which moves on by the same amount from each cell to the next. Each is labeled by a wave vector in the Brillouin zone, with as many of them, for each kind of state, as the crystal has cells.

III. Bands and Gaps

For most of its notes a piano strikes not one string but three, tuned as nearly alike as the tuner can make them, and all three rest on one wooden bridge. Through the bridge each string shakes the others a little, and the three, joined in this way, ring not at one pitch but at three pitches very close together. A single string has one note, and strings joined have a

cluster of notes about it, wider the more strongly they are joined. What becomes of the sharp energy levels of a single atom when very many atoms are joined in a crystal?

Start with N atoms of one kind standing in a lattice, but so far apart that no electron's wave reaches from one to the next. Each atom has its own levels, the separate levels of Volume One, Chapter 7, and each level of the single atom is found N times over, once on each atom, all at one energy. Now bring the atoms to their places in the crystal. The wave of an electron in a level of one atom now reaches a little onto its neighbors, and an electron can pass from one atom to the next. Volume One, Chapter 11, finds the same thing for two atoms sharing electrons in a bond: one level of each atom becomes two levels of the pair, a lower one, the bonding state, and a higher one. For N atoms the one level becomes N levels.

Bloch's theorem, the result of Section II, says which N. The states of definite energy are those in which the electron's wave on each atom is the wave of the single atom's level, turned forward by the phase ka from each atom to the next, with k taking its N values in the Brillouin zone. Their energies differ with k, because the waves on neighboring atoms meet in step where ka is near zero and out of step where ka is near half a turn. Waves that meet in step on the ground between two atoms lower the energy, as in the bonding state, while waves that meet out of step raise it. Take atoms in a row, each reaching only to its two neighbors, with E_0 the level of the single atom and t the energy with which an electron's wave on one atom reaches its neighbor. The energy is then $E(k) = E_0 - 2t\cos(ka)$ (standard physics of solids; Ashcroft and Mermin, 1976). As k runs over the zone, the energy runs over a range 4t wide. So each level of the single atom becomes, in the crystal, a *band*: the set of electron states in a crystal that grow from one state of the single atom. There are N of them, so close together in a large crystal that they fill a range of energy. The more the waves of neighboring atoms overlap, the larger t and the wider the band.

The deep levels of an atom, whose waves stay close to their own nucleus, become narrow bands, and the outer levels, whose waves reach far, become wide ones.

A second picture comes from the other end, from an electron that is almost free. In a metal such as sodium, the outer electron of each atom is held so weakly that its wave in the crystal is nearly a free wave, with energy $\hbar^2k^2/(2m_e)$, m_e being the electron's mass, rising smoothly with k. The free wave runs through the crystal undisturbed except at one kind of wavelength. Chapter 5, Box 5.1, found that a crystal turns a wave into a strong beam sent back from its planes when twice the spacing of the planes is a whole number of wavelengths. For a wave meeting a row of atoms a distance a apart head on, the first such wavelength is 2a, the wave vector $k = \pi/a$ at the edge of the Brillouin zone. There the electron's wave is sent back by every atom in step, and a wave running one way and its reflection running the other add into a *standing wave*, one whose crests stay in place. Two standing waves can be made at that wavelength. One has its crests on the atoms, where the electron is drawn close to the positive ions and its energy is lowered. The other has its crests between the atoms, and its energy is raised. So at the edge of the zone the energy jumps: below the jump the lower standing wave ends one band, and above it the upper standing wave begins the next. Between the two bands the crystal has no state at all (Brillouin, 1930).

Both pictures give the same result. The states of an electron in a crystal come in bands, one for each state of the single atom, and between two bands there may lie a range of energy in which the crystal has no electron state at all. Such a range is a *band gap*, or simply a *gap*: a range of energy with no electron state in the crystal.

A gap is found wherever no band reaches into the range between two bands, and in three dimensions bands can reach past one another. A crystal reaches in three directions, and its Brillouin zone has edges in many directions, with the jump at the edge coming at different energies in different directions. If the top of one band, in some direction, lies higher than

the bottom of the next band, in another direction, the two bands overlap in energy, and between them there is no gap. Whether two bands overlap depends on how wide they are and how far apart the levels they grew from lie, and so on the atoms and their spacing. Bloch's theorem fixes that there are bands, and the atoms fix where each band lies. Section V finds that this overlap is why magnesium and calcium are metals.

So we now know the shape of an electron's states in a crystal. Each sharp level of the single atom becomes a band of as many states as the crystal has cells, wider the more the atoms' waves overlap. Between bands lie gaps with no state, wherever no band reaches across.

IV. Filling the Bands

A crystal's electrons now have their states. How many electrons does a band hold, and where does the filling stop?

The electrons fill the states as fermions do. Chapter 2, Section XII, found that fermions fill the states open to them one to a state, from the lowest up to a top. At the lowest temperature every state below the top is full and every state above it is empty. The full states are called the *Fermi sea*, and the energy of the top is the *Fermi level*. The electron is a fermion of spin one half, so it is found with its spin along any chosen axis as one of two values, up or down. No two electrons share one state, by exclusion (Volume One, Chapter 1, Box 1.2). Box 6.2 counts what that means for a band.

Box 6.2. A band holds two electrons for each cell of the repeat

Premises. (1) A band of a crystal of N cells holds one state of the electron's motion for each value of the wave vector k in the Brillouin zone, and there are N such values (Box 6.1; Section III). (2) An electron, of spin one half, has two states of spin, up and down, for each state of its motion (Volume One, Chapter 7, Section VI). (3) No two electrons share one state: exclusion, derived from the principle of identity, "what no comparison can dis-

tinguish, in any way at all, even in principle, is one thing and not two" (*The Quantum Passage*, Chapter 8, Section VI; Volume One, Chapter 1, Box 1.2).

Steps. By (1) and (2), a band has $N \times 2 = 2N$ states in all. By (3), each holds at most one electron, so a band holds at most 2N electrons. A crystal of N cells holds 2N electrons in each full band: two for each cell.

Result. Each band holds two electrons, of opposite spin, for each cell of the repeat, the smallest block whose copies fill the crystal. The count is a count of states and holds for every crystal, whatever its atoms; which bands are full, and whether the last one is full, depends on how many electrons each cell brings.

So the electrons of a cold crystal fill its bands from the lowest up, two for each cell in each band, until every electron has a state. The filling stops somewhere, at the Fermi level, and Section V finds that where it stops decides whether the solid conducts. First, though, the simplest case can be worked through to the end, because it shows the Fermi sea of a metal directly.

In sodium, copper and the other metals whose atoms each give one loosely held electron to the whole crystal, the band those electrons fill behaves nearly as if the electrons were free. Its energy rises as $\hbar^2k^2/(2m_e)$ over most of the zone (Section III). Arnold Sommerfeld put Drude's free electrons together with the filling of fermions in 1928 (Sommerfeld, 1928), and the result is still the first account of a metal. The electrons fill every state of the motion with a wave vector shorter than some k_F, two to each, so the filled states make a ball in the space of wave vectors. The energy at its surface is the Fermi level, measured from the bottom of the band. That energy, for a free-electron metal, is called its *Fermi energy*. Box 6.3 finds it from the number of electrons in each unit of volume.

Box 6.3. The Fermi energy of copper

Premises. (1) In a box of volume V, one particle has $V\,d^3k/(2\pi)^3$ states of its motion for each small range d^3k of wave vectors, so the states with wave vectors shorter than k_F, a ball of volume $(4\pi/3){k_F}^3$, number $V\,{k_F}^3/(6\pi^2)$ (standard quantum mechanics; Chapter 2, Box 2.4, counts the same states by momentum, $p = \hbar k$). (2) Each state of the motion holds two electrons, one of each spin (Box 6.2). (3) An electron of the band moves as a free electron, with energy $\hbar^2k^2/(2m_e)$ (the free-electron model of Sommerfeld, 1928). (4) Copper's density is 8.935 grams for each cubic centimeter at 20 degrees Celsius, the mass of a mole of its atoms 63.546 grams, and each atom gives one electron to the band; the Avogadro constant is $6.02214076 \times 10^{23}$ for each mole (standard atomic weights; the density as tabulated). (5) $\hbar = 1.054571817... \times 10^{-34}$ joule seconds; $m_e = 9.1093837 \times 10^{-31}$ kilograms; the Boltzmann constant $k = 1.380649 \times 10^{-23}$ joules for each kelvin (the values recommended in 2022 by the Committee on Data of the International Science Council, CODATA).

Steps. By (1) and (2), N electrons in volume V fill the ball out to $2 \times V\,{k_F}^3/(6\pi^2) = N$, so $k_F = (3\pi^2 n)^{1/3}$, with $n = N/V$ the number of electrons in each unit of volume. By (3), the Fermi energy is $E_F = \hbar^2{k_F}^2/(2m_e) = \hbar^2(3\pi^2 n)^{2/3}/(2m_e)$. By (4), copper has $n = 8.935/63.546 \times 6.02214 \times 10^{23} = 8.47 \times 10^{22}$ free electrons in each cubic centimeter, 8.47×10^{28} in each cubic meter (computed). By (5), $k_F = 1.36 \times 10^{10}$ per meter and $E_F = 7.03$ eV; the electrons at the top move at the speed $\hbar k_F/m_e = 1.57 \times 10^6$ meters a second; and the temperature at which kT would equal E_F is 81,600 kelvin (computed).

Result. The Fermi energy of a free-electron metal is $E_F = \hbar^2(3\pi^2 n)^{2/3}/(2m_e)$, set by the number of free electrons in each unit of volume alone. For copper it is 7.03 eV, and the fastest of its electrons move at about half of one percent of the speed of light, even in a crystal at the lowest temperature.

The Fermi energy of a metal is large: 7.03 eV for copper, against the 0.026 eV of kT at room temperature. The electrons at the top of copper's Fermi sea move at 1.57 million meters a second even at the lowest temperature, because exclusion leaves them no slower state to go to. The speed of the top electrons of copper's Fermi sea is the cost of confinement of Volume One, Chapter 7, met in a new setting. No two electrons share a state, so the many electrons of a metal must take states of ever shorter waves, and the last ones in take states of high momentum.

The number of states in each small range of energy, near a given energy, is the *density of states*. For free electrons it grows as the square root of the energy, since the surface of the ball of filled states grows as k_F grows. At the Fermi level it comes to $3n/(2E_F)$ in each unit of volume and each unit of energy (mathematics, from Box 6.3). That number decides how the metal answers anything that disturbs it gently, and the first such disturbance is heat.

Think of a theater filled from the front, one person to a seat, with every seat taken up to some row and every seat behind it empty. Someone who wants to move can move only to an empty seat, and a person far forward in the crowd has every seat within reach taken. Only the people in the last few occupied rows can step back into the empty rows behind them. The electrons of a metal are in that theater. Warming the metal by a temperature T offers each electron energies of about kT. An electron deep in the Fermi sea could take up such an amount only by moving to an empty state within kT above it, and every state there is full. Only the electrons within about kT of the top can take up heat, a share of about kT/E_F of them, 0.0037 for copper at room temperature (computed). So the energy the electrons of a metal take up for each kelvin is in proportion to the temperature, $C = \gamma T$, with γ, read "gamma", set by the density of states at the Fermi level. For N free electrons, $C = (\pi^2/2)Nk(kT/E_F)$ (Sommerfeld, 1928). The heat capacity $C = \gamma T$ of the electrons is the *electronic heat capacity*, the electrons' share of the energy a metal takes up for each rise of one unit in temperature.

For copper, the free-electron count gives $\gamma = 0.503$ thousandths of a joule for each mole and each kelvin squared (computed from Box 6.3). The measured value is 0.695 (Kittel, 1996), larger by the factor 1.38 because copper's electrons answer as if a little heavier than free ones (Section VII). At room temperature the electrons then take up 0.21 joules for each mole and each kelvin, less than one percent of the lattice's 24.94. That answers the second question of Section I, why the electrons of a metal take up almost no heat, and it is why the Dulong-Petit law of Chapter 5 holds for metals as well as for insulators. But the lattice's part falls as the cube of the temperature (Chapter 5, Box 5.3), and the electrons' only as its first power, so in the cold the electrons win. For copper, whose Debye temperature is 343 kelvin, the two parts are equal at about 3.8 kelvin, and below that the electrons take up most of the heat (computed). Chapter 5, Section V, said that this part, in proportion to the temperature, outlasts the lattice's at the lowest temperatures, and here is its reason.

So we now know how the bands fill: two electrons for each cell in each band, from the bottom up to the Fermi level. In a free-electron metal that level lies several electron volts up, 7.03 eV in copper. Only the electrons within kT of it can take up heat, which makes the electrons' heat capacity small and in proportion to the temperature.

V. Metals and Insulators

A sliding-tile puzzle is a square frame with fifteen numbered tiles in a grid of sixteen squares, with one square left empty. A tile next to the empty square can slide into it, which leaves its own square empty, and so the tiles can be moved about the frame one at a time. Put a sixteenth tile into the empty square and the frame is packed full. Push on any tile as hard as you like, and every tile stays where it is, because every square is taken. Take out half the tiles, and almost every tile can move at the first touch. Where does a crystal's filling of its bands leave it: packed full, or with room to move?

A voltage across a crystal pushes on every electron in it alike. In a band, that push changes each electron's crystal momentum at the same steady rate, so that every electron's wave vector moves through the Brillouin zone in the direction of the push (standard physics of solids; Ashcroft and Mermin, 1976). Now look at two cases, as the puzzle shows them.

If the Fermi level falls inside a band, so that the band is only partly filled, there are empty states just above the filled ones. Then the smallest push moves electrons into them. The filled states shift a little toward the push in the space of wave vectors, more electrons move one way than the other, and charge flows. The solid conducts, and it conducts at once, however small the voltage.

If the Fermi level falls exactly at the top of a band, with a gap above, every state of the band is taken. The push still moves every wave vector along, but an electron leaving the zone at one edge comes back in at the other, since wave vectors that differ by a point of the reciprocal lattice are one state (Box 6.1). Every state stays taken, and the set of filled states is the same set as before. For every electron moving one way there is still one moving the other way, and the charge stays where it is. To carry charge, an electron would have to be lifted across the gap into the empty band above, which takes more energy than a small push gives. The solid holds back the current: it is an *insulator*. Alan Wilson gave this account of metals and insulators in 1931, three years after Bloch's theorem (Wilson, 1931).

A *metal*, in the language of bands, is then a solid whose Fermi level lies inside a band, and an insulator one whose bands are each either full or empty, with a gap above the last full one. Which a solid is depends on where the filling stops, and where it stops depends on how many electrons each cell of the crystal brings. Box 6.2 found that each band holds two electrons for each cell. That gives a rule of counting.

In the band picture, an odd number of electrons in each cell of the repeat leaves a band partly filled, since bands that hold two for each cell take up only even numbers exactly. Such a solid conducts. Sodium, with eleven electrons to each atom and one atom to each cell, is a metal, and so are copper, with twenty-nine, and aluminum, with thirteen. However the bands lie, overlapping or apart, an odd count fills no whole number of them.

The one way an odd count gives an insulator is through the electrons' push on one another, which the band picture leaves out. Where the band is narrow and the electrons repel one another strongly, an electron that hops onto an atom that already has one must pay the energy of their push. If that cost is larger than the band's width, the electrons stop hopping, each staying at its own atom, and the solid holds back the current. Such a solid is a *Mott insulator*, after Nevill Mott, who explained nickel oxide in this way in 1949 (Mott, 1949). Nickel oxide's cell, one atom of nickel and one of oxygen, holds thirty-six electrons, an even count. Its last electrons, though, only half fill the bands they enter, since two bands of nickel's d shell lie there at one energy and hold four electrons for each cell, of which nickel oxide brings two (standard physics of solids). So the bands alone would make nickel oxide a metal, and the push of its electrons on one another makes it an insulator, as it does for the odd count of the next example. Jan de Boer and Evert Verwey had pointed out in 1937 that a number of oxides of the transition metals are insulators though the bands say they should conduct (de Boer and Verwey, 1937). Cobalt oxide is one of them: each cell of its repeat, one atom of cobalt and one of oxygen, holds thirty-five electrons, an odd count, and it is an insulator.

An even number of electrons in each cell can fill a whole number of bands exactly, and then two cases are possible. If a gap lies above the last full band, the solid is an insulator. Diamond and silicon, each with two atoms in each cell of the repeat, twelve electrons in diamond's cell and twenty-eight in silicon's, have a gap above their last full band, 5.47 eV in diamond and 1.12 eV in silicon (Sze and Ng, 2007). If the last band that would be full overlaps the band above it, electrons fill the lower states of

both, both are left partly filled, and the solid conducts. Magnesium and calcium, with even counts, are metals for this reason. Figure 6.1 shows sodium, magnesium, silicon and diamond side by side.

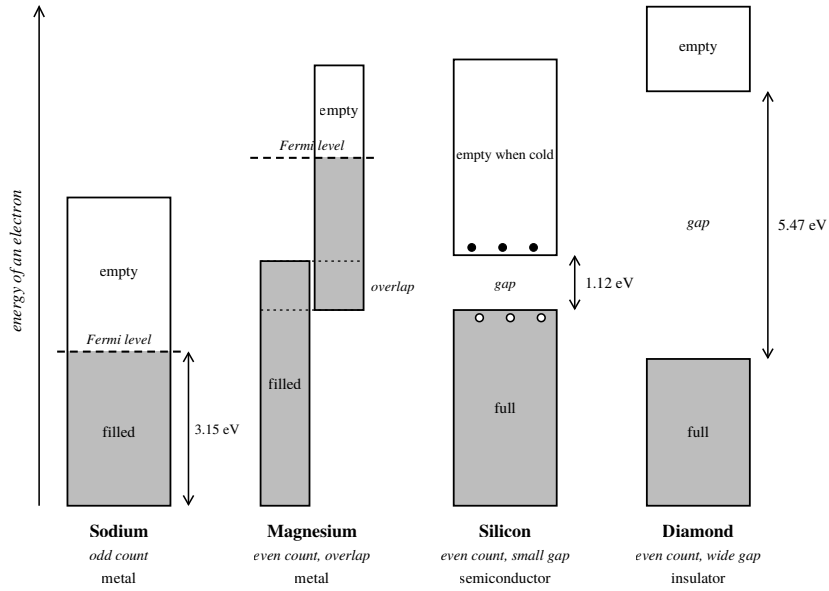


Figure 6.1. The bands of four solids, energy upward, filled states shaded. Sodium, with an odd count of electrons in each cell, fills its outer band only part way, to a Fermi level 3.15 eV above the band's bottom (computed as in Box 6.3), and is a metal. Magnesium, with an even count, has two bands that overlap in energy, so both are partly filled, and it is a metal. Silicon and diamond, with even counts, fill their last band exactly, with gaps of 1.12 eV and 5.47 eV above it (Sze and Ng, 2007), drawn to scale. At room temperature silicon has a few electrons lifted across its gap (dots) and as many empty states left behind (rings), and diamond has practically none. The gaps and sodium's filling are drawn to scale, and the widths of the bands and magnesium's overlap are drawn to show their order only.

The repeat itself can change, and with it the count. A crystal with an odd count in each cell can lower its energy, as it cools, by pairing its atoms, each moving a little toward one neighbor and away from the other. The repeat then becomes twice as long and holds twice the electrons. The count in the new cell is even, a gap opens at the Fermi level, and the solid becomes an insulator (Peierls, 1955). The chains of carbon atoms of the plastic polyacetylene pair in this way into alternating shorter and longer bonds. The spins of the electrons can do the same. In some crystals, as they cool, the spins on neighboring atoms come to point in opposite directions, an alternating magnetic order whose repeat is twice the crystal's, which again doubles the count in each cell. Chapter 8 takes up such orders of spins.

So we now know why metals conduct and insulators do not. A partly filled band lets the smallest push move electrons, and a full band with a gap above holds every electron to its set of states. An odd count in each cell leaves a band partly filled, except where the electrons' push on one another holds each at its own atom. An even count gives an insulator where a gap lies above the last full band and a metal where the bands overlap.

VI. Semiconductors

An electronic fever thermometer can hold in its tip a bead of a solid whose resistance falls steeply as it warms, called a thermistor, and read the temperature from that resistance, as the first such thermometer did in 1954 (standard accounts of the medical thermometer). Copper does the opposite: its resistance rises as it warms. The bead is a *semiconductor*, a solid with a full band and a gap above it, like an insulator, but with a gap small enough that heat lifts a few electrons across. How can a solid with a full band conduct at all, and why more when warm?

In silicon the last full band is called the *valence band*, since its states grew from the outer, bonding states of the atoms, and the empty band above it is called the *conduction band*. Between them lies the gap of 1.12 eV. At the lowest temperature silicon is an insulator, its valence band full and its conduction band empty. At room temperature heat offers each state energies of about kT, 0.026 eV, forty-three times less than the gap. That lifts an electron across seldom, but it lifts some. Their share is given by the Boltzmann factor of Chapter 2, Section X, the weight $e^{-E/kT}$ with which a part of a system is found in a state of energy E above its lowest.

Each electron lifted across does two things. It enters the empty conduction band, where every state about it is free, so a push moves it, as an electron in a metal's band is moved. And it leaves an empty state behind in the valence band, so that band is no longer full, and its other electrons can now move too, into the empty state, as the tiles of the puzzle can move once one square is free. Both carry charge, and so the solid conducts. Section VII finds that the empty state moves as a positive charge.

How many are lifted? The lifting of an electron across the gap is a change that runs both ways: a full valence band turns into an electron in the conduction band and an empty state in the valence band, and an electron falling back undoes it. Chapter 3's law of mass action holds for every such change that settles in balance, since its derivation in Chapter 3, Box 3.2, uses only the chemical potentials of what goes in and what comes out, whatever they are. So the amounts of what goes in and of what comes out stand in a fixed ratio set by the temperature. The amount of what goes in, a full band of some 10^{23} electrons, hardly changes. So the product of the numbers of electrons and of empty states, n and p, is fixed by the temperature through the Boltzmann factor of the whole gap: $n \times p = N_c N_v e^{-E_g/kT}$ (standard physics of semiconductors; Sze and Ng, 2007). Here E_g is the gap, and N_c and N_v are the numbers of states, in each unit of volume, that the two bands offer within about kT of their edges. In a pure semicon-

ductor every electron lifted leaves one empty state, so n = p, and each goes as $e^{-E_g/2kT}$, the Boltzmann factor of half the gap. Such a solid, conducting by its own lifted electrons alone, is an *intrinsic* semiconductor.

For silicon at 300 kelvin, $e^{-E_g/2kT}$ is 3.9×10^{-10} (computed). The measured number of lifted electrons is 1.0×10^{10} in each cubic centimeter (Sproul and Green, 1991), among 5×10^{22} atoms: one electron lifted for each five million million atoms. With so few lifted electrons, pure silicon conducts more than a hundred thousand million times less well than copper. The same factor makes the number climb steeply with temperature. From 300 to 350 kelvin, the number of lifted electrons in silicon grows about twenty-eight times (computed, with the numbers of states growing as $T^{3/2}$), and the resistance falls accordingly, which is what the thermometer reads. In diamond, with its gap of 5.47 eV, the factor at room temperature is e^{-106}, about 10^{-46} (computed), and diamond is an insulator.

So the difference between a semiconductor and an insulator is one of size, not of kind. Both have a full band with a gap above, and the gap's size against kT decides whether heat lifts enough electrons to matter. A semiconductor conducts more as it warms because more electrons are lifted across its gap, each leaving an empty state that moves as well. A metal conducts less as it warms, for a reason Section VIII gives.

VII. How an Electron Moves in a Band, and the Empty States

A rowboat pushed off from a dock moves as if it were heavier than it is, because it cannot move without pushing some of the water around it along too. Something moving inside a medium answers a push with a mass that the medium helps to set. How does an electron in a band answer a push, and how does an empty state in a full band move?

An electron in a band answers a push through its band. Its speed is set by how steeply the band's energy rises with the wave vector, $v = (1/\hbar)dE/dk$, and a steady push changes its wave vector at a steady rate (Sec-

tion V). So how fast its speed changes under a push depends on how sharply the band curves, its *curvature*, the rate at which its slope changes with the wave vector (standard physics of solids; Ashcroft and Mermin, 1976). Near the bottom of a band, every band curves upward as a bowl does, and its energy there can be written as $\hbar^2k^2/(2m^*)$. Near the bottom of a band, the band's energy has the form of a free electron's energy with the electron's mass replaced by m*, the electron's *effective mass*. The effective mass is the mass with which an electron in a band answers a push, set by the band's curvature. A wide band, whose atoms' waves overlap strongly, curves sharply and gives a light effective mass, and a narrow band gives a heavy one. In gallium arsenide the electrons at the bottom of the conduction band answer as if their mass were 0.067 of a free electron's. In silicon the effective mass differs with direction, 0.98 of the electron's mass along one axis and 0.19 across it (Sze and Ng, 2007). The effective mass belongs to the electron in that band of that crystal, and the electron itself keeps its own mass, charge and spin.

Near the top of a band the curve turns over, and there the band's energy falls as k moves away from the top. An electron near the top of a band therefore answers a push as if its mass were negative: pushed one way, its speed changes the other way, because the push carries its wave vector toward states where the band is less steep. The strange answer of an electron near the top of a band, as if the electron's mass were negative, is what makes the empty states of a nearly full band simple.

Go back to the sliding-tile puzzle with one square empty. When a tile slides left into the empty square, the empty square moves right. Watching fifteen tiles each move once is a complicated way to describe what happened, and watching the one empty square move is simple. A nearly full band is the same. A full band carries no current, since for every electron moving one way another moves the other (Section V). So the current of a band with one electron missing is the current of the full band, which is none, less the current the missing electron would carry. The band as a whole answers a push exactly as that one missing electron would, with its charge reversed (mathematics, from the full band's zero current). The

missing electron sat near the top of the band, where its effective mass was negative. Reverse its charge and its mass together, and what is left is a positive charge with a positive mass.

So an empty state in a nearly full band moves as a particle with positive charge and positive mass. Such an empty state is called a *hole*. A hole is a collective excitation of the electrons of the band, a motion of all of them at once described as the motion of one missing electron. It exists only in the band of a crystal, as the phonon of Chapter 5, Section IV, exists only in a crystal's lattice, and so it stands apart from the kinds of particle. In a semiconductor warmed by heat (Section VI), both the lifted electrons and the holes they leave carry current, the electrons as negative charges and the holes as positive ones, and the two currents add.

That holes carry positive charge can be seen, as well as counted. Lay a flat strip of the solid on a table, run a current along it, and hold a magnet below it so that its magnetic field passes up through the strip. A magnetic field pushes a moving charge sideways, at right angles to its motion. So the *carriers of charge*, the electrons or holes that carry the current, are crowded toward one edge of the strip, and a small voltage appears across its width. A carrier of charge is a second sense of the word "carrier", apart from the carriers of the forces of Chapter 1. In this chapter and the next it always means a carrier of charge. Which edge they crowd toward depends on the sign of their charge. For a given current, negative carriers moving one way and positive carriers moving the other way are pushed toward the same edge, so they charge that edge with opposite signs. The voltage that appears across the strip's width is the *Hall effect*, which Edwin Hall found in 1879 (Hall, 1879). In a semiconductor whose carriers are mostly electrons the Hall voltage has the sign of negative carriers. In one whose carriers are mostly holes it has the sign of positive carriers, and so do some metals, whose Fermi level lies near the top of a band (standard physics of solids). The size of the voltage gives the number of carriers in each unit of volume. Hall sensors read magnetic fields from that voltage in many machines, from the timing of a car engine's sparks to the closing of a telephone's cover (standard accounts of Hall sensors).

So we now know how electrons and empty states move in a band. An electron near the bottom of a band answers a push as a free particle of the band's effective mass, set by its curvature. An empty state near the top of a nearly full band moves as a positive charge with positive mass, a hole, which the Hall effect shows directly.

VIII. Why a Perfect Crystal Does Not Resist

Walk through an orchard planted in perfect rows. Down any aisle between the rows you can walk as far as the orchard goes and never meet a tree, however many trees there are. Plant one tree out of line, and the walker in that aisle must turn aside. Let a wind set every tree swaying, and the aisles are never quite clear. Only a tree out of its place stands in the way, and the trees in their rows leave every aisle clear. Drude's electrons bumped into the ions. Why, then, do the electrons of copper pass a hundred and fifty of them before anything turns them aside?

Bloch's theorem has already answered. A Bloch state is a state of definite energy of an electron in the whole crystal, and it already has the crystal's repeated form, the same in every cell up to its phase (Box 6.1). A state of definite energy stays as it is in time, changing only by a phase that changes no finding (standard quantum mechanics). So an electron in a Bloch state of a perfect crystal whose atoms stand still keeps that state, with its wave vector and its speed, for as long as the crystal stays perfect and still. The regular array of ions, which Drude took for the obstacle, is built into the state itself, so it turns no electron aside. A perfect, motionless crystal offers no resistance.

Resistance comes from departures from perfect repeat. There are two kinds in every real crystal. The first kind of departure from perfect repeat is the crystal's motion: the crystal's atoms vibrate about their places, in the phonons of Chapter 5, Section IV. A lattice whose atoms are momentarily displaced is repeated only imperfectly, so it turns electrons from one Bloch state into another, an electron giving up or taking in a phonon. The

second kind of departure from perfect repeat is the crystal's flaws: atoms of another element, vacancies, dislocations and the boundaries between grains (Chapter 5, Section VI), each a tree planted out of line. The phonons grow in number as the crystal warms, and above its Debye temperature the number in each mode grows in proportion to the temperature (Chapter 5, Section V). So a metal's resistance from them rises in proportion to the temperature: copper's resistance rises by about 0.4 percent for each kelvin near room temperature (standard tables of resistivity). The flaws stay the same at every temperature. As a metal is cooled, its phonons freeze out and their part of the resistance falls away, until only the flaws are left. The resistivity then settles at a floor, the *residual resistivity*, which is lower the purer and the more perfect the crystal. Augustus Matthiessen found in the 1860s that the parts add, the flaws' part the same at every temperature and the vibrations' part the same for every sample of a metal (Matthiessen and Vogt, 1864). That addition is *Matthiessen's rule*.

A question remains: the electrons push on one another, so do they resist one another, even in a perfect, motionless crystal? Two electrons that meet and turn each other aside keep their total crystal momentum, as two balls that collide keep their total momentum. In a band of nearly free electrons the current is set by the electrons' total momentum. So an ordinary collision between electrons only passes momentum from one electron to another and leaves the current as it was. The electrons' push on one another, by itself, has the crystal's own repeated form, and it leaves the current on its course. But crystal momentum is kept only up to a point of the reciprocal lattice (Section II). In some collisions between two electrons the crystal as a whole takes up one such step of momentum, as it does when it sends an X-ray into a strong beam by Bragg's law. Then the two electrons' total momentum changes, and the current is turned back. Rudolf Peierls named such a process an *umklapp*, German for a flipping over, since the electrons' wave vectors pass the edge of the Brillouin zone and reappear at the other side (Peierls, 1929). So electrons colliding with electrons, the crystal taking up the momentum, do resist, even in a perfect crystal. Since only electrons within about kT of the Fermi level can collide, both elec-

trons of a pair must lie in that thin layer of the Fermi sea. So the resistance this gives grows as the square of the temperature at low temperature (Landau and Pomeranchuk, 1936; Baber, 1937). It is found in very pure metals, below the temperatures where the phonons' part has fallen away. Like the phonons' part, it vanishes as the temperature goes to zero, so at the lowest temperature only the flaws resist.

Ohm's law now follows. A voltage across a wire makes an electric field that pushes every electron's wave vector along at a steady rate (Section V). Each departure from perfect repeat, a phonon, a flaw or an umklapp collision, turns an electron back into the crowd of the Fermi sea after an average time τ, read "tau". Between turnings an electron gains a drift in the direction of the push in proportion to the field and to τ. So the current, the number of electrons in each unit of volume times their charge times their drift, is in proportion to the field. The resistivity is $m^*/(ne^2\tau)$, with n the number of free electrons in each unit of volume and e the size of their charge (Drude, 1900, in the form the bands give it). For copper, with n from Box 6.3 and the measured resistivity at 20 degrees Celsius, τ comes to 2.5×10^{-14} seconds. An electron at the Fermi level, moving at 1.57×10^6 meters a second, then goes about 39 nanometers between turnings, some hundred and fifty times the distance between neighboring copper atoms, which is 0.256 nanometers (computed, with the free electron's mass for m^*). Meanwhile the drift itself is slow. A current of one ampere through a copper wire of one square millimeter moves the electrons along at 0.07 millimeters a second (computed), though each of them is moving at 1,570 kilometers a second in its own state.

The same electrons carry heat. Where one end of a copper bar is hotter than the other, the electrons near the Fermi level at the hot end are more stirred than those at the cold end. They carry energy along the bar, turned aside by the same phonons and flaws that resist the current. So a metal that conducts charge well conducts heat well. Where the electrons carry both, and each turning stops the carrying of charge and of heat alike, the ratio of the two is the same for every metal. The thermal conductivity κ,

read "kappa", divided by the electrical conductivity σ, read "sigma", the inverse of the resistivity, and by the temperature, is $(\pi^2/3)(k/e)^2 = 2.44 \times 10^{-8}$ watt ohms for each kelvin squared (computed; Sommerfeld, 1928). Gustav Wiedemann and Rudolph Franz found in 1853 that good conductors of electricity are good conductors of heat, in the same order (Franz and Wiedemann, 1853). Ludvig Lorenz found in 1872 that the ratio grows in proportion to the temperature, and the whole is the *Wiedemann-Franz law*. For copper at 0 degrees Celsius the measured ratio is 2.23×10^{-8} (Kittel, 1996). Copper's 401 watts for each meter and each kelvin (Chapter 5, Section V) are therefore carried by copper's electrons, far more than by copper's phonons: the heat goes the way the current goes.

So we now know why a perfect crystal does not resist and what does. An electron in a Bloch state keeps its state in a perfect, motionless crystal. Resistance comes from the crystal's vibrations, from its flaws and from collisions of electrons in which the crystal takes up the momentum. All but the flaws vanish at the lowest temperature, and the same electrons and the same turnings set a metal's conduction of heat.

IX. Clear, Shining and Colored Solids

A window is clear. A polished wafer of silicon is gray, shining and opaque. Cadmium yellow, the painter's pigment, is a powder of cadmium sulfide. A copper coin is reddish, a gold ring yellow and a silver spoon white. Light falls on all of them alike. Why does each solid take some light and pass or send back the rest?

Light comes in photons: the *photon*, the particle of light, carries the electric force between charges. Each photon of light of frequency f carries the energy hf, with h the Planck constant. The light the eye sees runs from about 1.65 eV at the red end to about 3.26 eV at the violet end, wavelengths from 750 to 380 nanometers (standard physics). A solid takes up a photon only if the photon's energy can lift an electron from a filled state to an empty one. A photon also carries momentum, but so little

against the crystal momenta of a band that the electron's wave vector hardly changes when it takes one up. So the electron is lifted straight upward in energy, at nearly the same k (standard physics of solids).

In a solid with a full band and a gap above it, a photon whose energy is less than the gap finds no empty state within reach of any electron. Such photons pass through. Window glass is made mostly of silica, whose gap of about 9 eV (Tropf, Harris and Thomas, 2000) is far above every photon of visible light, so glass is clear. Diamond, with its gap of 5.47 eV, is clear for the same reason. Silicon's gap of 1.12 eV lies below every photon of visible light, so silicon takes up all visible light that enters it and is opaque. Its polished surface also sends back a large share of the light that falls on it, and so it shines gray (Chapter 11 takes up why a surface sends light back). But photons of infrared light with less than 1.12 eV, wavelengths longer than 1,107 nanometers (computed), pass through silicon. In between lie the colored semiconductors. Cadmium sulfide's gap of 2.42 eV takes up violet, blue and part of the green, every photon above 2.42 eV, wavelengths shorter than 512 nanometers (computed), and passes the rest, so it looks yellow. For a semiconductor, then, the gap sets the color. Table 6.1 gives the gaps of the solids this chapter and the next use.

Table 6.1. Band gaps at 300 kelvin (Sze and Ng, 2007), the wavelength at which each solid begins to take up light (hc divided by the gap, computed), and whether the gap is direct or indirect (see the text).

Solid	Gap (eV)	Takes up light shorter than	Gap	Seen as
Germanium	0.66	1,879 nm (infrared)	indirect	gray, opaque
Silicon	1.12	1,107 nm (infrared)	indirect	gray, opaque
Gallium arsenide	1.42	873 nm (infrared)	direct	gray, opaque
	2.42	512 nm (green)	direct	yellow

Cadmium sulfide				
Gallium nitride	3.4	365 nm (ultraviolet)	direct	clear
Diamond	5.47	227 nm (ultraviolet)	indirect	clear

The last column but one of the table carries a difference that matters in the next chapter. In gallium arsenide the top of the valence band and the bottom of the conduction band lie at the same wave vector, at the center of the Brillouin zone. So a photon with the gap's energy can lift an electron straight across: such a gap is *direct*. In silicon the bottom of the conduction band lies at another wave vector from the top of the valence band, and an electron lifted across the smallest gap must change its crystal momentum as well. The photon carries too little momentum to supply it, so a phonon must be taken up or given out at the same moment: such a gap is *indirect*. A process that needs a photon and a phonon together is far slower than one that needs a photon alone. So silicon takes up light weakly just above its gap, and, run the other way, an electron falling back across silicon's gap gives out light only rarely. Chapter 7 finds that this is why the lamps made from semiconductors are not made from silicon.

Just below the gap, a solid can take up light that the bands alone would not allow. An electron lifted across the gap and the hole it leaves attract each other, a negative charge and a positive one. They can be bound together, as the electron and the proton of the hydrogen atom are, into a pair that moves through the crystal as one: an *exciton*. Its energy levels lie below the bottom of the conduction band, in a series like hydrogen's. The series is far shallower and larger than hydrogen's, made so by the solid's weakening of the electric pull and by the band's effective masses, as Chapter 7, Box 7.1, works out for an electron bound to a single added atom. In cuprous oxide, a red oxide of copper, the series has been followed up to the level $n = 25$, where a single exciton extends over more than two

micrometers (Kazimierczuk, Fröhlich, Scheel, Stolz and Bayer, 2014). The exciton's lowest level there extends over about a nanometer, so the crystal holds a hydrogen-like series of levels made inside it.

A metal, with its partly filled band, has empty states just above its filled ones, and a photon of any energy finds an electron to lift. But a metal's free electrons answer light all together. Chapter 4, Section IX, found that free electrons together ring at their plasma frequency, $\omega_p = \sqrt{(ne^2/(\varepsilon_0 m_e))}$, set by the number of free electrons in each unit of volume, their charge and their mass. Here ε_0 is the electric constant of that chapter. Light of lower frequency than that sets the free electrons swinging all together in time with it, and their swing sends the light back. Below its plasma frequency a metal reflects, and that is its shine. Light of higher frequency changes direction too fast for the electrons to follow, and it passes: above its plasma frequency a metal is clear. So a metal sends back light only below its plasma frequency. For copper, with the electron density of Box 6.3, the plasma frequency corresponds to photons of 10.8 eV and a wavelength of 115 nanometers, far in the ultraviolet (computed), so a metal sends back all visible light. For sodium, whose free electrons are fewer, it corresponds to a wavelength of 210 nanometers (computed from its density, 0.9688 grams for each cubic centimeter). Robert Wood found in 1933 that thin films of sodium, opaque to visible light, become clear in the ultraviolet below 210 nanometers (Wood, 1933). Chapter 11 follows light into matter in full, and takes up what the plasma frequency does to it there.

The colors of copper and gold come from a second source. Below their free electrons' band these metals have full, narrow bands grown from the atoms' d states, and a photon of enough energy can lift an electron from one of them into an empty state above the Fermi level. In copper that begins near 2 eV, in the orange (Ehrenreich and Philipp, 1962). So copper takes up some of the green, blue and violet light that falls on it and sends back more of the red and orange, and looks reddish. Gold's begins a little higher, in the green, and gold looks yellow. In silver the same lifting be-

gins in the ultraviolet, near 4 eV, so silver sends back all visible light alike and looks white. Other colors of solids have other sources still (standard physics of color; Nassau, 1983). A ruby is red because a few chromium ions in its crystal of aluminum oxide take up green and violet light, between their own levels, though the crystal's gap is far wider than any visible photon. A crystal of salt struck by X-rays turns yellowish brown because electrons trapped at vacancies, called *color centers*, take up blue light. And dyes take their colors from the levels of their molecules. The gap sets the color of a semiconductor, the d bands set the colors of copper and gold, and ions, flaws and molecules set many of the other colors of the solids in the world.

So we now know why solids are clear, shining or colored. A solid takes up a photon only if the photon can lift an electron to an empty state. So a solid with a gap passes light below its gap, is clear if the gap is wider than visible light, and is colored by its gap if the gap falls within it. A metal sends back light below its plasma frequency and passes light above it, and the colors of copper and gold come from their deeper bands.

In Use

The wires of a house are copper because copper is, after silver, the metal that resists least: 1.678×10^{-8} ohm meters at 20 degrees Celsius against silver's 1.59×10^{-8} (standard tables of resistivity). Silver's high cost keeps it for special uses (standard accounts of copper conductors). The measured resistivity is copper's own, and I give the reasons for that resistivity. Copper has an odd count, one free electron for each atom in a half-filled band (Section V). Its Fermi energy of 7.03 eV gives the electrons at the top of its Fermi sea a speed of 1.57 million meters a second (Box 6.3). And in a well-made copper wire those electrons go about 39 nanometers between turnings at room temperature, turned aside mostly by the vibrations of the lattice (Section VIII). A wire warms as it carries current, because each turning hands energy to the lattice, and its resistance rises as it warms, by

about 0.4 percent for each kelvin. Wire for power is drawn from copper made very pure, since every atom of another element in it is a tree out of line.

Aluminum resists more than copper, 2.65×10^{-8} ohm meters, so a wire of it must be about 1.6 times thicker in cross-section to carry the same current with the same loss. But aluminum's density is 2.70 grams for each cubic centimeter against copper's 8.935, so the thicker aluminum wire weighs only about half as much as the copper one (computed). The lighter weight of the aluminum wire is why the long lines that carry power across the country are made mostly of aluminum, wound round a core of steel for strength (standard accounts of overhead power cables). The long lines hang from towers, where every kilogram must be held up. Inside a building, where the thinner wire fits more easily and weight matters less, the wiring is copper.

The screen of a telephone answers a finger, and the screen of a computer turns each small region light or dark. Both need a layer that conducts across the whole screen and yet lets the light through. A metal sends back every photon of visible light, since its plasma frequency lies in the ultraviolet (Section IX), so a layer of metal would hide the screen. The answer is a *transparent conductor*, and the commonest is indium tin oxide, indium oxide with a little tin in it. Its gap is about 4 eV, wider than any photon of visible light, so it passes visible light as glass does. The tin atoms each give up an electron to the conduction band of the indium oxide, as I explain in Chapter 7, so it conducts, with a resistivity near 10^{-6} ohm meters, some sixty times copper's (Kim et al., 1999). Its free electrons are far fewer than a metal's, so its plasma frequency lies in the infrared, below visible light: a film of it passes visible light and sends back the infrared. A film a fraction of a micrometer thick passes more than four-fifths of visible light. Films of indium tin oxide are the clear electrodes of liquid-crystal displays (Chapter 4, In Use), of touch screens and of solar panels. The same film on window glass sends heat back into a room while letting

daylight in. Two results of this chapter make it work: a gap wider than visible light keeps it clear, and a plasma frequency below visible light keeps it from shining like a metal.

Summary

The electrons of a crystal take states that are set by the crystal's repeat. Because a shift by one step of the lattice leaves the crystal and its laws unchanged, the states of an electron of definite energy can be chosen in a special way. Each, shifted by one step, is the same state turned forward by a phase that is the same at every step: Bloch's theorem (Box 6.1). Such a state belongs to the whole crystal, and it is labeled by a wave vector in the Brillouin zone, with as many values as the crystal has cells. $\hbar k$ is its crystal momentum, kept in every change up to a point of the reciprocal lattice. Each state of the single atom becomes a band of such states, wider the more the atoms' waves overlap. Between bands lie gaps with no state wherever no band reaches across, and in three dimensions bands may overlap, closing the gap between them. Each band holds two electrons, of opposite spin, for each cell of the repeat (Box 6.2).

The electrons fill the bands from the bottom up to the Fermi level, and where the filling stops determines how the solid conducts. A partly filled band lets the smallest push move electrons, so the solid is a metal. A full band with a gap above holds every electron to its set of states, so the solid is an insulator. An odd count of electrons in each cell leaves a band partly filled, so the solid conducts, except where the electrons' push on one another holds each at its own atom, a Mott insulator. An even count gives an insulator where a gap lies above the last full band, as in diamond and silicon, and a metal where the bands overlap, as in magnesium and calcium. A crystal can also double its repeat on cooling, by pairing its atoms or by an alternating order of spins, which turns an odd count into an even one. In a free-electron metal the Fermi energy is set by the density of electrons, 7.03 eV in copper (Box 6.3). Only electrons within kT of it take up heat, so

the electrons' heat capacity is small and in proportion to the temperature. A semiconductor is an insulator with a small gap. Heat lifts electrons across in numbers set by the Boltzmann factor of half the gap, 1.0×10^{10} in each cubic centimeter of silicon at 300 kelvin, and both the lifted electrons and the holes they leave carry current, more as the solid warms. An electron in a band answers a push with an effective mass set by the band's curvature. An empty state near the top of a band moves as a positive charge, a hole, a collective excitation that the Hall effect shows directly.

A perfect, motionless crystal offers no resistance, since a Bloch state already has the crystal's repeated form and keeps its state. Resistance comes from the crystal's vibrations, from its flaws and from collisions of electrons in which the crystal takes up a step of momentum. All of these but the flaws vanish at the lowest temperature, which leaves the residual resistivity. From the time between turnings Ohm's law follows. The electrons that carry the current also carry heat, so the conduction of heat and of charge in a metal stand in the ratio of the Wiedemann-Franz law. A solid takes up a photon only if the photon can lift an electron to an empty state. A solid with a gap passes light below its gap, so the gap sets the clearness and the color of a semiconductor. A metal sends back light below its plasma frequency and passes it above. Copper and gold take their colors from their deeper bands, and ions, flaws and molecules give many other solids theirs.

In silicon, heat supplies one free electron for every five million million atoms, and the number is fixed by the temperature. A semiconductor's few carriers of charge can be added on purpose, by an added atom whose pull on its electron I work out in the next chapter. What can be built from that?

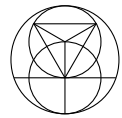
✶

KEY CONCEPTS

- **Current; voltage; resistance; Ohm's law.** Charge passing a point each second; the energy each unit of charge gains or gives up between two points; the ratio of voltage to current; and the proportion of current to voltage in most solids.
- **Resistivity.** The resistance of a cube of a material one meter on a side, between opposite faces: 1.678×10^{-8} ohm meters for copper, 7.5×10^{17} for fused quartz.
- **Free-electron model.** A metal pictured as fixed ions with a gas of free electrons (Drude), filled as fermions fill their states (Sommerfeld).
- **Bloch's theorem; Bloch state.** The states of an electron of definite energy in a crystal can be chosen so that each, shifted by one step of the lattice, is the same state turned forward by a phase that is the same at every step (Box 6.1); such a state belongs to the whole crystal.
- **Phase.** The stage of a wave's swing at a place, counted as a fraction of a whole turn (the wave sense, apart from the phases of matter of Chapter 4); a factor that turns a wave's swing forward by a fixed fraction of a turn everywhere changes no finding.
- **Crystal momentum; Brillouin zone.** $\hbar k$ for a Bloch state of wave vector k, kept in every change up to a point of the reciprocal lattice; and the single cell of the reciprocal lattice, centered on zero, in which every state's wave vector can be placed.
- **Band.** The set of electron states in a crystal that grow from one state of the single atom, as many as the crystal has cells, wider the more the atoms' waves overlap.

- **Band gap.** A range of energy with no electron state in the crystal; it lies between two bands wherever no band reaches across, and overlapping bands leave none.
- **Standing wave.** A wave whose crests stay in place, made by a wave and its reflection; at the edge of the Brillouin zone two of them, at different energies, bound a gap.
- **Fermi sea; Fermi level; Fermi energy.** The filled states of the electrons at the lowest temperature, and the energy of the top of them; for a free-electron metal, that energy measured from the bottom of its band, 7.03 eV for copper (Box 6.3).
- **Density of states.** The number of states in each small range of energy near a given energy.
- **Electronic heat capacity.** The electrons' share of the energy a metal takes up for each rise of one unit in temperature, in proportion to the temperature, because only electrons within kT of the Fermi level can take up heat.
- **Metal; insulator.** A solid whose Fermi level lies inside a band; and one whose bands are each full or empty, with a gap above the last full one.
- **Mott insulator.** A solid whose bands alone would leave a band partly filled, and which holds back the current because its electrons repel one another so strongly that each stays at its own atom.
- **Semiconductor; valence band; conduction band; intrinsic semiconductor.** An insulator with a gap small enough that heat lifts a few electrons across; its last full band and the empty band above; and a semiconductor conducting by its own lifted electrons alone.
- **Effective mass.** The mass with which an electron in a band answers a push, set by the band's curvature.
- **Hole.** An empty state in a nearly full band, which moves as a positive charge with positive mass; a collective excitation of the band's electrons, apart from the kinds of particle.
- **Carrier of charge.** An electron or a hole that carries a current (a second sense of "carrier", apart from the carriers of the forces of Chapter 1).

- **Hall effect.** The voltage across a strip carrying a current in a magnetic field, whose sign shows the sign of the carriers of charge.
- **Residual resistivity; Matthiessen's rule.** The resistivity left at the lowest temperature, from flaws alone; and the adding of the parts of the resistivity from flaws and from vibrations.
- **Umklapp.** A collision of electrons in which the crystal takes up a step of momentum equal to a point of the reciprocal lattice, so that the current is turned back even in a perfect crystal.
- **Wiedemann-Franz law.** The ratio of a metal's conduction of heat to its conduction of charge, divided by the temperature, is $(\pi^2/3)(k/e)^2$, the same for every metal whose electrons carry both.
- **Direct and indirect gaps.** A gap whose band edges lie at one wave vector, so a photon alone can lift an electron across; and one whose edges lie at different wave vectors, so a phonon must take part.
- **Exciton.** An electron and a hole bound together by their electric pull, in hydrogen-like levels just below the gap.
- **Color center.** An electron trapped at a vacancy of a crystal, which takes up light of one color.
- **Transparent conductor.** A solid with a gap wider than visible light and enough free electrons to conduct, with a plasma frequency in the infrared, such as indium tin oxide.



Chapter 7

Semiconductors at Work

CHAPTER OVERVIEW

A diode passes current one way, and a transistor switches a large current with a small action. Both are built by setting a semiconductor's carriers of charge, its electrons and holes, on purpose. An added atom with one more outer electron than silicon's, such as phosphorus, holds its extra electron as a hydrogen atom would, with the binding weakened and the size enlarged by the crystal. The binding is the Rydberg energy, 13.606 eV, the binding of one electron held by a fixed charge of the proton's size (Chapter 1, Box 1.4), times $(m^*/m_e)/\varepsilon^2$ (Box 7.1). Here m^* is the band's effective mass and ε the dielectric constant, the factor by which the solid weakens the electric pull. That gives 0.026 eV for silicon against 0.045 eV measured for phosphorus, with the electron's wave a few nanometers across. Its level lies just below the conduction band, and at room temperature, by Saha's rule, almost every such atom, a donor, gives its electron to the band. An atom with one fewer, such as boron, gives a hole. Silicon so doped is n-type, its carriers mostly electrons, or p-type, its carriers mostly holes, and the product of its electrons and holes is fixed by the temperature. Where p-type meets n-type, carriers wander across and fill one another, leaving a depletion layer whose fixed charges build a barrier, 0.71 volts in the example. There the Fermi level, the electrons' chemical potential, is the same on both sides (Figure 7.1). A voltage that lowers the barrier, a forward voltage, lets the majority carriers, the kind the doping supplies, climb it in numbers that grow by the Boltzmann factor. A

voltage that raises it leaves only the small flow of minority carriers, the few of the other kind: $I = I_0(e^{eV/kT} - 1)$, the diode law (Box 7.2). In the field-effect transistor of every chip, a voltage on an electrode called the gate, acting through a thin insulating oxide, draws a channel of electrons between two n-type regions and so switches the current between them on and off. A chip holds billions of them. In a direct-gap semiconductor a forward-biased junction gives out light whose color is set by the gap, the light-emitting diode (LED). Light above the gap taken up at a junction is carried off as current, in the solar cell and in each pixel, each smallest point, of a camera's image, and one junction turns at most about 30 percent of sunlight into power.

I. One Way Only

Chapter 6 ended with a question: a semiconductor's few carriers of charge can be added on purpose, so what can be built from that?

The valve of a bicycle tire lets air in when the pump pushes and holds it there when the pump stops: it passes a flow one way only. Electricity has its own such valve. In 1874 Ferdinand Braun found that a fine metal point pressed on a crystal of a metal sulfide passed current far more readily one way than the other (Braun, 1874). From 1906 on, crystals of silicon touched by a fine wire, the "cat's whiskers" of the first radio sets, picked the sound out of radio waves by passing their current one way only (Pickard, 1906). A device that passes current one way and holds it back the other way is a *diode*, and passing current one way only is called *rectifying* it. Today a diode is made by joining two kinds of silicon inside one crystal. Three such layers make a *transistor*, a device in which a small current or voltage at one place switches or controls a much larger current elsewhere, and a computer chip holds billions of transistors.

So the reader's question is this: how does a diode pass current one way, and how does a transistor switch?

In Chapter 6 we found nearly everything the answer needs. A semiconductor is a solid with a full band, the valence band, and an empty band above it, the conduction band, separated by a gap small enough that heat lifts a few electrons across. In pure silicon at room temperature there are 1.0×10^{10} lifted electrons in each cubic centimeter, with as many empty states, called holes, left behind in the valence band. A *hole* moves as a positive charge, and an electron in the conduction band as a negative one. Both are carriers of charge in the sense of Chapter 6, Section VII. Two things are still needed: a way to set the number of carriers at will, and an account of what happens where two regions with different carriers meet. In this chapter we supply both, and then build the diode, the transistor, the lamp that turns current into light and the cell that turns light into current.

II. Carriers Added on Purpose

Picture a class of children lined up for a walk, every child hand in hand with partners on both sides, so that the whole class forms one linked chain and no child is free. Add one child who has an extra hand and nobody to take it: that child can be drawn away from the chain at the smallest tug. Add instead a child with one hand too few, and there is a gap in the chain, into which a neighbor can reach, leaving a gap one place along. How can a few added atoms of another element supply a semiconductor with carriers?

Silicon stands in the column of the periodic table whose atoms have four outer electrons. In its crystal each silicon atom is joined to four neighbors by four *covalent bonds*, each a bond made by a pair of electrons shared between two atoms, and those shared pairs fill the valence band exactly (Chapter 6, Section V). Put in place of one silicon atom an atom of phosphorus, the next element along, with five outer electrons. Four of them make the four bonds, as silicon's would, and the fifth has no bond to join. It is held to the phosphorus atom only by the one extra positive charge

that the phosphorus nucleus has over a silicon nucleus. So the fifth electron and the extra charge make something like a hydrogen atom, sitting inside the crystal: one positive charge and one electron, held by the electric pull alone.

But it is a hydrogen atom changed in two ways by the crystal around it. First, the crystal weakens the pull. The silicon atoms between the electron and the phosphorus ion are pulled slightly out of shape by the ion's electric field, their electrons shifting a little toward it, and that shift partly cancels the ion's charge as seen from farther away. The pull is weakened by a factor called the solid's *dielectric constant*, the factor by which a solid weakens the electric pull between two charges placed in it, 11.7 for silicon (standard tables of the properties of silicon). Second, the electron moves in the conduction band, so it answers the pull with the band's effective mass (Chapter 6, Section VII) in place of the free electron's mass. In Volume One, Chapter 7, we found hydrogen's size and binding from the balance of the cost of confinement against the pull, and in this volume we restate that balance in Chapter 1, Box 1.4. In Box 7.1 we carry the balance over to the electron of a phosphorus atom in silicon.

Box 7.1. The donor as a scaled hydrogen atom

Premises. (1) An electron of mass m held by a pull $F = \alpha\hbar c/r^2$ to a fixed charge has the least extent $a = \hbar/(mc\alpha)$ and the binding $\alpha^2 mc^2/2$, from the balance of the cost of confinement against the pull; for the free electron's mass m_e these are the Bohr radius $a_0 = 0.0529$ nanometers and the Rydberg energy, 13.606 eV, the binding hydrogen would have if its proton did not move at all (Volume One, Chapter 7, Box 7.1; this volume, Chapter 1, Box 1.4). (2) Inside a solid of dielectric constant ε, read "epsilon", the pull between two charges at a distance large against the spacing of the atoms is weakened to $F = \alpha\hbar c/(\varepsilon r^2)$ (standard electromagnetism of solids). (3) An electron in the conduction band answers a pull with the band's effective mass m*, in place of m_e (Chapter 6, Section VII). (4) For silicon, $\varepsilon = 11.7$; the effective mass of its conduction electrons, averaged over the directions of their motion, is $m^* = 0.26\ m_e$, from $0.98\ m_e$ along

one axis and 0.19 m_e across it; and the side of its cubic cell is 0.543 nanometers, with 5×10^{22} atoms in each cubic centimeter (standard tables of the properties of silicon; Sze and Ng, 2007).

Steps. By (2), the pull is that of (1) with α replaced by α/ε; by (3), the mass is m* in place of m_e. So by (1) the binding is $(\alpha/\varepsilon)^2 m^* c^2/2 = 13.606$ eV $\times$ $(m^*/m_e)/\varepsilon^2$, and the extent is $a_0 \times \varepsilon/(m^*/m_e)$. By (4), for silicon: 13.606 eV $\times$ $0.26/11.7^2 = 0.026$ eV, 526 times less than the 13.606 eV of premise (1), and the extent is $0.0529 \times 11.7/0.26 = 2.4$ nanometers (computed). That extent is 4.4 times the side of silicon's cubic cell, and a sphere of that radius holds about 2,800 silicon atoms (computed), so the electron's wave reaches over very many atoms, as premise (2) requires.

Result. An atom with one more outer electron than the atoms of the crystal binds that electron as a hydrogen atom would, with the binding weakened and the size enlarged by the crystal: binding 13.606 eV $\times$ $(m^*/m_e)/\varepsilon^2$, a few hundredths of an electron volt, and size $a_0\varepsilon/(m^*/m_e)$, a few nanometers. For phosphorus in silicon the scaled hydrogen gives 0.026 eV and 2.4 nanometers; the measured binding is 0.045 eV (Sze and Ng, 2007), and the measured extent about 2.5 nanometers (Zwanenburg et al., 2013). Both lie far below the gap of 1.12 eV: the electron's level lies just below the bottom of the conduction band.

The scaled hydrogen atom gives the size of the donor electron's wave and the scale of its binding, and the binding found by measurement is larger than the scaled value by less than a factor of two. The difference comes from the part of the wave closest to the phosphorus atom. There the electron is within a few atoms of the ion, where the crystal's weakening of the pull, which needs many atoms between the charges, applies only in part. And the phosphorus core itself holds the electron a little more tightly than a point charge would. So, measured or scaled, the extra electron of a phosphorus atom is held by a few hundredths of an electron volt, some twenty-five times less than the gap, and its level lies just below the conduction band, ready to enter it. An atom added to a crystal to supply an

electron in this way is a *donor*. The adding of a small, chosen amount of another element to a semiconductor, to set its carriers, is *doping*, and the added atoms are *dopants*.

At room temperature almost every donor gives up its electron. That follows from the rule we found in Chapter 2, Box 2.4, for the hydrogen of the early universe, Saha's rule. An electron freed from its atom has far more ways to be than a bound one, so the free electrons win even when kT is well below the binding. Here kT is 0.026 eV and the binding 0.045 eV, so the Boltzmann factor of the binding is 0.18. And the conduction band offers about 3×10^{19} states for each cubic centimeter within reach of kT of its bottom (standard tables of the properties of silicon). For phosphorus added at 10^{16} atoms for each cubic centimeter, one for every five million silicon atoms, Saha's rule then leaves 99.6 percent of the donors with their electrons given to the conduction band (computed). Silicon doped in this way holds 10^{16} free electrons in each cubic centimeter, a million times the 10^{10} that heat alone lifts across the gap. It conducts several hundred thousand times better than pure silicon, whose current is carried by its 10^{10} electrons and its 10^{10} holes together. A semiconductor whose carriers are mostly electrons given by donors is *n-type*, n for negative.

The child with one hand too few is the other case. Put in place of a silicon atom an atom of boron, from the column before silicon's, with three outer electrons. Three of the four bonds are made, and the fourth lacks an electron. An electron from a neighboring bond can move into it, which leaves the gap one bond along: that is a hole. The hole is held near the boron atom, which now carries one extra negative charge, by the same weakened pull, and freed from it by a few hundredths of an electron volt: for boron in silicon, 0.045 eV (standard tables of the properties of silicon). An atom added to supply a hole in this way is an *acceptor*, since it accepts an electron from the valence band. A semiconductor whose carriers are mostly holes given by acceptors is *p-type*, p for positive.

In doped silicon both kinds of carrier are present, but in very unequal numbers. In Chapter 6, Section VI, we found by the law of mass action that the product of the numbers of electrons and holes is set by the temperature alone. In silicon at 300 kelvin, $n \times p = (1.0 \times 10^{10})^2 = 10^{20}$ for each cubic centimeter squared, whatever has been added. So in n-type silicon with 10^{16} electrons in each cubic centimeter there are only 10^4 holes, since every added electron that meets a hole fills it. The carriers of the kind the doping supplies are the *majority carriers*, and the few of the other kind are the *minority carriers*. The minority carriers, as we find in Section IV, are what lets a junction pass a small current backward.

So we now know how carriers are added on purpose. An atom with one more outer electron than silicon's holds that electron as a hydrogen atom would, its binding weakened by the crystal's dielectric constant and the band's effective mass to a few hundredths of an electron volt. So at room temperature it gives the electron to the conduction band. An atom with one fewer gives a hole in the same way, and the numbers of electrons and holes are set by the doping, with their product fixed by the temperature.

III. Where p Meets n

Open a bottle of perfume in one room of a house with the door to the next room open, and in time the scent reaches the next room too, though no draft carries it. Its molecules, each moving at random, wander from where they are many to where they are few, until they are as many on both sides of the door. Now suppose that each molecule carried an electric charge, and that the molecules of a second kind, with the opposite charge, were wandering the other way. What happens where a region of p-type silicon meets a region of n-type silicon in one crystal?

A *p-n junction* is the boundary, inside one crystal, between a region doped with acceptors and a region doped with donors. It is made by doping one part of a silicon crystal one way and the next part the other way,

so the crystal itself runs on unbroken through the boundary, and only the dopants change. On the n side the conduction band holds many free electrons, and on the p side the valence band holds many holes. Both kinds of carrier wander by their random motion from where they are many to where they are few, as the perfume does. This wandering is *diffusion*. So electrons wander from the n side into the p side, and holes from the p side into the n side, and where an electron meets a hole it falls into it, and both are gone.

But the carriers leave something behind. Each electron that leaves the n side leaves a donor ion, a phosphorus atom that has given up its electron and so carries a positive charge, fixed in its place in the crystal. Each hole that leaves the p side leaves an acceptor ion with a negative charge, also fixed. So a layer forms on both sides of the boundary that is emptied of carriers and holds the fixed charges of the dopants: positive on the n side, negative on the p side. That layer is the *depletion layer*. Its charges make an electric field across it, pointing from the n side to the p side, which pushes electrons back toward the n side and holes back toward the p side. The more carriers cross, the larger the charge left behind and the stronger the field, until the field's push back just balances the wandering, and the crossing stops on average.

Where does the balance settle? In Chapter 2, Section XI, we found that particles pass from where their chemical potential is higher to where it is lower until it is equal. The *chemical potential* of a kind of particle is the energy that adding one more particle of that kind brings to the system. For the electrons of a solid, the chemical potential is the energy at which a state is as likely to be full as empty, by the filling of fermions of Chapter 2, Box 2.5. At the lowest temperature that energy is the top of the filled states, the Fermi level of Chapter 6, Section IV, and the chemical potential keeps the name Fermi level at every temperature. In a semiconductor it can lie inside the gap, where there are no states, since it marks where the filling is half and half, whether or not any state lies there. On the n side the Fermi level lies near the conduction band, since electrons are many there, and on the p side it lies near the valence band, since electrons are

few. In balance the Fermi level must be the same on both sides, so the bands themselves must shift. The field of the depletion layer raises every electron's energy on the p side, relative to the n side, by just enough to bring the two Fermi levels into line. That shift makes a *barrier* in the sense of Chapter 3, Section II, an arrangement of highest energy along the way. An electron at the bottom of the n side's conduction band must climb by the amount of the shift to reach the bottom of the p side's, and the amount is the height of the junction's barrier.

The barrier can be counted. On each side the number of electrons in the conduction band goes as the Boltzmann factor of the distance from the Fermi level up to the band. So the ratio of the electron numbers on the two sides, N_{don} on the n side and n_i^2/N_{acc} on the p side, is the Boltzmann factor of the barrier. Here N_{don} and N_{acc} are the numbers of donors and acceptors in each unit of volume, written so to keep them apart from the Avogadro constant N_A. And n_i is the number of electrons that heat alone lifts across the gap in pure silicon, so that n_i^2/N_{acc} is the number of minority electrons on the p side, by the law of mass action (Section II). So the barrier, divided by the charge of an electron to give a voltage, is $(kT/e)\ \ln(N_{acc}N_{don}/n_i^2)$, with ln the natural logarithm, the logarithm to the base e = 2.718 (standard physics of semiconductors; Sze and Ng, 2007). For silicon doped with 10^{16} donors on one side and 10^{16} acceptors on the other, in each cubic centimeter, at 300 kelvin, it is 0.02585 volts × $\ln(10^{12})$ = 0.714 volts, 0.71 volts to two places (computed). The depletion layer is then 0.43 micrometers thick, and the field across it reaches 3.3 million volts for each meter at the boundary (computed from the charge of the dopants and silicon's dielectric constant). Figure 7.1 shows the bands across such a junction, without a voltage and with one.

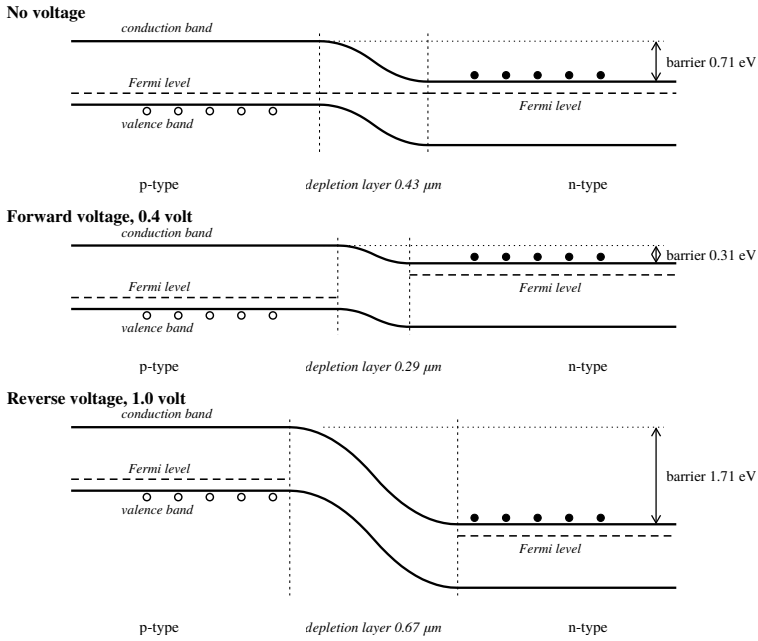


Figure 7.1. The bands across a silicon p-n junction with 10^{16} acceptors on the p side (left) and 10^{16} donors on the n side (right) in each cubic centimeter, at 300 kelvin. Electron energy runs upward, drawn to scale in energy (gap 1.12 eV) and in distance. Dots are electrons in the conduction band of the n side, and rings are holes in the valence band of the p side. Without a voltage (top) the Fermi level (dashed) is the same throughout, and the bands rise 0.71 eV from the n side to the p side across a depletion layer 0.43 micrometers thick, bounded by the dotted lines. A forward voltage of 0.4 volt (middle) lowers the barrier to 0.31 eV and thins the layer to 0.29 micrometers, so many more electrons climb it. A reverse voltage of 1.0 volt (bottom) raises the barrier to 1.71 eV and widens the layer to 0.67 micrometers. With a voltage the Fermi levels of the two sides differ by the voltage times the electron's charge. Values computed in Section III and Box 7.2.

The barrier is a voltage built into the crystal, and it stays inside it. A wire joining the two ends of the junction finds the same Fermi level, the energy that matters to the electrons of the wire, on both sides, and so finds no voltage between them. The barrier sorts the carriers. Electrons on the n side and holes on the p side, the majority carriers, are held back by it. Electrons on the p side and holes on the n side, the few minority carriers, are carried across it by its field. In balance the two flows match, and the net current is zero.

So we now know what happens where p meets n. Carriers wander across and fill one another, leaving a thin layer emptied of carriers that holds the fixed charges of the dopants. The field of those charges builds a barrier, 0.71 volts in the example, at which the Fermi level is the same on both sides and the crossing stops on average.

IV. The Diode Law

A weir across a river holds the water back, and only the water above the weir's crest flows over it. Lower the crest a little, and the flow over it grows by far more than the small lowering would suggest, because so much more of the river now stands above the crest. Raise the crest, and the flow over it soon stops. What does a voltage applied across a junction do to its barrier, and to the current?

Connect a battery to the junction. Nearly all of the battery's voltage falls across the depletion layer, since that layer has almost no carriers and so resists far more than the doped regions on either side. If the battery's positive end is joined to the p side, the voltage lowers the barrier: this is *forward bias*. If its positive end is joined to the n side, the voltage raises the barrier: this is *reverse bias*. In Box 7.2 we follow the two flows of Section III when the barrier is moved.

Box 7.2. The diode law

Premises. (1) Across a junction in balance, with no voltage applied, electrons of the n side climb the barrier into the p side, and the few minority electrons of the p side are carried down the barrier into the n side by its field; the two flows are equal, and no net current runs (Section III). (2) The share of the n side's electrons with energy enough to climb a barrier of height E above them is the Boltzmann factor $e^{-E/kT}$ (Chapter 2, Section X), since the electrons of the conduction band, few against its states, fill them as particles in the classical limit do. (3) The flow down the barrier is set by how many minority electrons reach the edge of the depletion layer on the p side, which depends on the doping and the temperature and not on the height of the barrier. (4) A voltage V across the junction, positive on the p side, lowers the barrier by eV; negative on the p side, it raises it by $e|V|$; e is the size of the electron's charge. (5) The same holds for holes, with p and n exchanged; their current adds to the electrons'.

Steps. Call the equal flows of (1) I_0, counted as currents. By (4) and (2), a voltage V multiplies the flow up the barrier by $e^{eV/kT}$, so it becomes $I_0e^{eV/kT}$. By (3), the flow down the barrier stays I_0. The net current is the difference: $I = I_0e^{eV/kT} - I_0$. By (5), holes give a current of the same form, and I_0 is the sum of the two.

Result. The current through a p-n junction is $I = I_0(e^{eV/kT} - 1)$: the *diode law* (Shockley, 1949). With a forward voltage the current grows as $e^{eV/kT}$: at room temperature, where $kT/e = 25.85$ millivolts, each 59.5 millivolts more multiplies it by ten (computed). With a reverse voltage of more than a few times kT/e the current is $-I_0$, the small flow of minority carriers, whatever the voltage.

A large current one way and almost none the other way is the one-way passing of the junction, and the one-way passing rests on the Boltzmann factor. Under forward bias the current climbs as an exponential. 0.3 volts across a silicon junction multiplies the forward flow a hundred thousand

times over its balance value, and 0.6 volts multiplies it twelve thousand million times (computed), which is why a silicon diode seems to switch on near 0.6 or 0.7 volts. Under reverse bias the current is the tiny flow I_0 of minority carriers, which are few: in n-type silicon with 10^{16} donors in each cubic centimeter, only 10^4 holes (Section II). So the junction passes current freely one way and hardly at all the other way: it is a diode. William Shockley gave this account of the junction in 1949 (Shockley, 1949), two years after the first transistor had been made. A reverse voltage large enough does at last break the junction down. The field in the depletion layer then speeds the few carriers enough to free others from their bonds, and the current rises sharply (standard physics of semiconductors). Diodes made to do this at a set voltage hold voltages steady in power supplies (standard accounts of the Zener diode, as such diodes are called).

Diodes turn the alternating current of a wall outlet into the steady current that a telephone's battery or a computer needs. The current of the outlet reverses a hundred or a hundred and twenty times each second, for mains of 50 or 60 swings a second (standard accounts of the frequency of the mains). A set of four diodes lets each half of the alternating wave through to the load in the same direction. A diode of two kinds of silicon in one crystal does the work of the cat's whisker of the first radio sets.

So we now know how a diode passes current one way. A voltage that lowers the junction's barrier lets the majority carriers climb it in numbers that grow as $e^{eV/kT}$, by the Boltzmann factor. A voltage that raises the barrier leaves only the small, fixed flow of minority carriers: $I = I_0(e^{eV/kT} - 1)$.

V. The Transistor

A drawbridge joins two banks of a river. Lowered, it carries all the traffic that comes, and raised, it carries none. The bridge-keeper who raises and lowers it does so with a small effort, however heavy the traffic. A switch of

that kind, in which a small action controls a large flow, is what every computer is built from, billions of times over. How can a crystal of silicon be made into such a switch?

The first transistor was made at Bell Laboratories in December 1947 by John Bardeen and Walter Brattain, with two fine gold contacts pressed on a crystal of germanium (Bardeen and Brattain, 1948). William Shockley worked out the junction transistor soon after (Shockley, 1949), and the three shared the Nobel Prize in Physics for 1956, for "researches on semiconductors and their discovery of the transistor effect" (Nobel Foundation, 1956). The junction transistor is a sandwich of three layers in one crystal, for example n-type, then a very thin p-type layer, then n-type again. The first junction is run with forward bias, so electrons pour from the first n layer into the thin p layer, in numbers set by the diode law of Box 7.2. The p layer is so thin that nearly all of them wander across it before they meet a hole, and reach the second junction, which is run with reverse bias. Its field, which holds back the majority carriers, carries these electrons, which are minority carriers in the p layer, straight across into the last n layer. So a large current runs through the whole sandwich, while only a small current runs into the middle layer, the one that keeps the thin p layer supplied with holes to replace those the electrons fill. A small change in that small current changes the large one many times over. A small current that changes a large current many times over is the transistor as an amplifier. A radio makes a faint signal loud with the transistor as an amplifier.

The transistor of a computer chip is of another kind, a switch worked by a voltage rather than a current: the *field-effect transistor*. Take a piece of p-type silicon and make two small n-type regions in its surface a short distance apart, the *source* and the *drain*. Between them the surface is p-type, so the path from source to drain runs through two junctions back to back. Whichever way a voltage is put across them, one of the two junctions has reverse bias and passes almost nothing: the switch is off. Over the stretch of surface between the source and the drain lies a very thin layer of silicon dioxide, an insulator whose gap of about 9 eV holds back the current

(Chapter 6, Section IX), and on top of that an electrode, the *gate*. Put a positive voltage on the gate. Its field reaches through the thin oxide into the silicon beneath, pushing the holes away from the surface and drawing electrons to it, the few minority electrons of the p-type silicon and others from the source and drain. Above a certain gate voltage, the *threshold*, the thin layer of silicon under the gate holds more electrons than holes. It has become n-type, a channel of electrons joining the n-type source to the n-type drain, and current flows between them. The switch is on. Take the gate voltage away, and the channel vanishes.

The gate is the bridge-keeper. It draws no steady current at all, since the oxide beneath it is an insulator. Turning the switch on or off costs only the small charge that sets the gate's voltage. Mohamed Atalla and Dawon Kahng made the first such transistor, of metal, oxide and silicon, at Bell Laboratories in 1959 (Computer History Museum, "1960: Metal Oxide Semiconductor (MOS) Transistor Demonstrated"). The same switch can be made the other way round, with an n-type body, p-type source and drain, and a channel of holes drawn by a negative gate voltage. Pairs of the two kinds, joined so that whenever one is on the other is off, make the circuits of nearly every chip (standard physics of semiconductor devices; Sze and Ng, 2007). A pair draws current only in the moment it switches, so billions of them can work together and the chip stays cool enough to run.

A switch that is on or off holds one of two values, and a chip computes by joining switches so that the state of some sets the state of others. The parts were first joined on one piece of semiconductor in 1958, when Jack Kilby built a working circuit with all its parts formed in semiconductor. In 1959 Robert Noyce conceived the circuit made wholly in one flat chip of silicon, its parts joined by aluminum lines laid over an insulating layer of oxide. The first working circuits of that kind were made at Fairchild Semiconductor in May 1960 (Computer History Museum, "1959: Practical Monolithic Integrated Circuit Concept Patented"). The *integrated circuit* is transistors, diodes and their connections made together in the surface of one chip of silicon by doping, oxidizing and depositing metal in patterns.

So we now know how a transistor switches. In a field-effect transistor the gate's voltage, acting through an insulating layer, draws a thin channel of electrons into the p-type silicon between two n-type regions and so joins them, and taking the voltage away removes the channel. In a junction transistor a small current into a thin middle layer controls a large current through all three.

VI. Light from a Junction

The small red light that shows a television is on, the white light of a modern flashlight, and the infrared flash of a remote control that changes its channel all come from p-n junctions. A junction with forward bias pushes electrons into the p side and holes into the n side, where they meet carriers of the other kind and fall into them. Where does the energy go when an electron falls into a hole?

An electron that falls from the bottom of the conduction band into a hole at the top of the valence band gives up about the energy of the gap. It can give it up as a photon, of energy close to the gap, or it can give it up to the lattice as heat, in phonons. In Chapter 6, Section IX, we found which. In a semiconductor with an indirect gap, such as silicon, the electron and the hole sit at different crystal momenta, and a photon alone carries too little momentum to take up the difference. So a phonon must take part, and the fall gives out light only rarely. In a semiconductor with a direct gap, such as gallium arsenide, the electron falls straight down, and most falls give out a photon. A junction made of a direct-gap semiconductor, run with forward bias, is a *light-emitting diode*, an LED: a diode that gives out light whose photons each carry about the energy of the gap.

So the color of an LED is set by its gap, and the gap is chosen by choosing the semiconductor. Gallium arsenide, with its gap of 1.42 eV, gives out infrared light near 873 nanometers (computed; Table 6.1), and infrared LEDs of gallium arsenide are the lights of remote controls. Mixing in other elements of the same columns of the periodic table changes the gap.

Gallium arsenide with some of its arsenic replaced by phosphorus gave the first visible red LEDs (Holonyak and Bevacqua, 1962). Gallium nitride has a gap of 3.4 eV, in the ultraviolet, and mixed with some indium its gap narrows into the blue: a gap of 2.7 eV gives light near 460 nanometers (computed from the gap). Bright blue LEDs of gallium nitride were made in the early 1990s by Isamu Akasaki, Hiroshi Amano and Shuji Nakamura, who received the Nobel Prize in Physics for 2014 (Nobel Foundation, 2014). Blue was the color that mattered most, because white light can be made from it. A blue LED coated with a layer of a phosphor that takes up part of the blue light and gives out yellow light in its place gives a mixture that the eye sees as white (standard physics of lighting).

An LED turns current into light with little loss, because each electron that crosses the junction can give one photon, of an energy set by the gap, and little of the energy goes elsewhere. The light a lamp gives, measured as the eye sees it, is counted in *lumens*, and its efficiency in lumens for each watt of power drawn. The best white LEDs have passed 300 lumens for each watt, against 16 for an ordinary filament bulb and close to 70 for a fluorescent lamp (Nobel Foundation, 2014). The same junction, made with mirrors at its two ends so that the light passes back and forth and each photon makes others like itself, is the semiconductor laser of a fiber-optic line and a barcode reader. In Chapter 11 we take up the laser, with the rest of light in matter.

So we now know how a junction gives light. Forward bias pushes electrons and holes together at the junction, and in a direct-gap semiconductor each electron that falls into a hole gives out a photon of about the gap's energy, so the gap sets the color.

VII. Light into Current

Run the LED backward. Shine light on a p-n junction, and the junction gives out current. How does a junction turn light into current, and how much of the light can it turn?

A photon whose energy is more than the gap, taken up near the junction, lifts an electron from the valence band to the conduction band, which leaves a hole behind: it makes a pair of carriers. If the pair is made in or near the depletion layer, the layer's field carries them apart, the electron to the n side and the hole to the p side, before they can meet again. Electrons gather on the n side and holes on the p side. If the two sides are joined by a wire through a lamp or a battery, the electrons run round through the wire to meet the holes, and the current does work on the way. A junction used in this way is a *photodiode*, and made large, to gather sunlight for power, it is a *solar cell*. The first practical silicon solar cell was made at Bell Laboratories in 1954 by Daryl Chapin, Calvin Fuller and Gerald Pearson (Chapin, Fuller and Pearson, 1954).

How much of the sunlight a cell can turn into power follows from what we found in Chapter 6 about the gap. A photon with less energy than the gap passes through without being taken up, so its energy is lost to the cell: in silicon, every photon of wavelength longer than 1,107 nanometers. A photon with more energy than the gap makes one pair. The electron and hole, made high in their bands, give up the energy above the gap edges to the lattice as heat, in phonons, within a very short time, and only about the gap's worth of each photon's energy is left to be used. And a warm cell glows, as every body at a temperature gives out the light of Chapter 2, Section XIII: some of its electrons and holes fall back together and give out light. The more carriers the sunlight gathers on the two sides, the higher the cell's voltage and the faster they fall back, since the falling back grows by the Boltzmann factor of the voltage, as the forward current of Box 7.2 does. The voltage settles where the falling back matches the making of pairs, and that lies below the gap (Shockley and Queisser, 1961). A wide gap wastes the photons below it, and a narrow gap wastes the energy of every photon above it. William Shockley and Hans Queisser counted the three losses together (the photons below the gap, the energy above it and the glow of the warm cell), treating sunlight as the light of a black body (Chapter 2, Section XIII). They found the most that one junc-

tion can turn into power: "The maximum efficiency is found to be 30% for an energy gap of 1.1 ev" (Shockley and Queisser, 1961). Silicon's gap of 1.12 eV lies at that best gap.

A camera's sensor is a field of photodiodes, one under each *pixel*, the smallest point of the image. Each photon taken up in a pixel frees one electron, and the pixel gathers the freed electrons while the shutter is open. Afterward the charge of each pixel is measured, and its size tells how much light fell there. Willard Boyle and George Smith invented the first electronic way to gather and read out the charges of many pixels quickly, the charge-coupled device, in 1969, and received the Nobel Prize in Physics for 2009 (Nobel Foundation, 2009). Most cameras now read each pixel through transistors made beside it on the same chip (standard accounts of the active-pixel sensor). Silicon takes up every photon of visible light, so it sees every color. It answers every color alike, so filters of red, green and blue are laid over neighboring pixels. Silicon also takes up near-infrared light, out to 1,107 nanometers, which the eye cannot see, so a camera carries a filter that stops it.

So we now know how a junction turns light into current. A photon above the gap makes an electron and a hole, the junction's field carries them apart, and they return through an outer circuit as a current. One junction can turn at most about 30 percent of sunlight into power, at a gap near silicon's.

In Use

A computer chip begins as a thin round slice cut from a single crystal of silicon, grown from melted silicon purified until other elements are a vanishing share of it. The purity is needed because stray atoms of the elements that act as donors and acceptors would set its carriers before the maker could. Into its surface the doping is then put on purpose (standard accounts of the making of chips). Ions of boron, phosphorus or arsenic are fired into chosen regions, and the crystal is heated so that they settle into

the places of silicon atoms in the lattice (in Chapter 5, Section VI, we found how atoms move through a solid by stepping into vacancies). Layers of oxide are grown and metal is laid down, region by region, in patterns printed by light. Each field-effect transistor of Section V is one source, one drain, one channel and one gate, and a chip holds very many. The processor that Apple introduced in 2020 holds 16 billion transistors, made in what its maker calls a 5-nanometer process (Apple, 2020). Every one of them works by the gap of Chapter 6, the donors and acceptors of Box 7.1 and the junctions of Box 7.2.

The white LED lamp that is taking the filament bulb's place is a blue junction of gallium nitride with indium, under a coat of phosphor (standard accounts of the LED lamp). It is run with forward bias by a small circuit that turns the alternating current of the wall outlet into a steady current with diodes. It gives several times the light of a filament bulb for each watt (Section VI). About a fourth of the electricity the world uses goes to lighting (Nobel Foundation, 2014), so that gain matters to the world's use of power.

A solar panel is a row of large silicon photodiodes, joined one after another so that their voltages add. Each is a thin slice of p-type silicon with a shallow n-type layer on the side facing the Sun and metal fingers to gather the current. Its silicon is used because silicon's gap lies near the best gap for one junction (Section VII), and because silicon is made pure and cheap in quantity for chips. And a solar cell, unlike an LED, works with an indirect gap: a thick enough slice takes up the light above silicon's gap, though less readily than a direct-gap semiconductor would. Cells made of two or more junctions stacked one on another, each with its own gap, take more of the sunlight than one junction can, because each photon is taken up by a junction whose gap lies just below its energy. Such cells power spacecraft (standard accounts of multi-junction cells).

The camera of a telephone holds a sensor of many millions of photodiodes on one chip of silicon, each with its own few transistors beside it, every pixel counting the electrons freed in it by light, through the same junction and the same gap. The chip, the LED lamp, the solar panel and

the camera sensor are four uses of one structure, the p-n junction, run four ways. It runs as a switch, forward to give light, and backward to gather light for power or for a picture.

Summary

A semiconductor's carriers can be set at will by doping. An atom with one more outer electron than the atoms of the crystal, such as phosphorus in silicon, holds its extra electron as a hydrogen atom would, with the binding weakened and the size enlarged by the crystal. Its binding is the Rydberg energy of 13.606 eV, the binding hydrogen would have if its proton did not move (Box 7.1). That energy is multiplied by the effective mass over the free electron's mass and divided by the square of the dielectric constant, which gives a few hundredths of an electron volt. The electron's wave is a few nanometers across. For phosphorus in silicon the scaled hydrogen gives 0.026 eV and 2.4 nanometers, and the binding measured is 0.045 eV. The measured binding is larger because, close to the phosphorus atom, its core pulls the electron a little more strongly than a point charge would. Either way the donor's level lies just below the conduction band, and at room temperature, by Saha's rule, almost every donor gives its electron to the band. An atom with one fewer outer electron, such as boron, gives a hole in the same way. Silicon doped with donors is n-type, with acceptors p-type, and in either the product of the numbers of electrons and holes is fixed by the temperature alone.

Where p-type meets n-type in one crystal, carriers wander across and fill one another, leaving a depletion layer that holds the fixed charges of the dopants. Their field builds a barrier, $(kT/e)\ \ln(N_{acc}N_{don}/{n_i}^2)$, 0.71 volts for the junction of Figure 7.1, at which the Fermi level is the same on both sides. A voltage that lowers the barrier lets the majority carriers climb it in numbers that grow by the Boltzmann factor. A voltage that raises it leaves only the small flow of minority carriers, so the current is $I = I_0(e^{eV/kT} - 1)$, the diode law (Box 7.2). The current grows ten times for

each 59.5 millivolts forward at room temperature, and it is a small fixed current backward. A transistor switches a large current with a small action. In the field-effect transistor of every chip, a voltage on a gate, through an insulating layer of oxide, draws a channel of electrons that joins two n-type regions. In the junction transistor, a small current into a thin middle layer controls a large current through three. A forward-biased junction in a direct-gap semiconductor gives out light whose color is set by its gap, the LED. Light above the gap taken up near a junction makes pairs that the junction's field carries apart into a current, in the photodiode, the solar cell and the camera's pixel. One junction turns at most about 30 percent of sunlight into power, at a gap near silicon's (Shockley and Queisser, 1961).

The semiconductors of this chapter are ordered in their atoms and free in their electrons. In other solids the electrons' spins, the angular momentum each carries in itself, with no motion along a path, come to point in one direction together, as the atoms of a crystal come to stand in rows. And in some ordered states of electrons, a quantity comes in steps of a fixed size. The Hall resistance of a thin sheet of electrons in a strong magnet rises in flat steps set by Planck's constant and the electron's charge (Chapter 10). Some solids order not their atoms but their spins. Why does iron hold a direction?

✶

KEY CONCEPTS

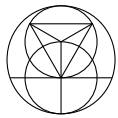
- **Diode; rectifying.** A device that passes current one way and holds it back the other way; passing current one way only.
- **Transistor.** A device in which a small current or voltage at one place switches or controls a much larger current elsewhere.
- **Dielectric constant.** The factor by which a solid weakens the electric pull between two charges placed in it; 11.7 for silicon.

- **Donor; acceptor.** An added atom with one more outer electron than the crystal's atoms, which gives that electron to the conduction band; and one with one fewer, which gives a hole to the valence band.
- **Doping; dopant.** The adding of a small, chosen amount of another element to a semiconductor to set its carriers; and an atom so added.
- **n-type; p-type.** A semiconductor whose carriers are mostly electrons from donors; and one whose carriers are mostly holes from acceptors.
- **Majority and minority carriers.** The carriers of the kind the doping supplies, and the few of the other kind; their numbers multiply to a product fixed by the temperature.
- **Diffusion.** The wandering of particles, by their random motion, from where they are many to where they are few.
- **p-n junction; depletion layer; barrier.** The boundary inside one crystal between p-type and n-type regions; the layer about it emptied of carriers, with only the fixed charges of the dopants left in it; and the barrier, the rise in electron energy across that layer, whose height is $(kT/e)\ \ln(N_{acc}N_{don}/n_i^2)$ as a voltage, with N_{acc} and N_{don} the numbers of acceptors and donors in each unit of volume.
- **Fermi level (at any temperature).** The electrons' chemical potential, the energy at which a state is as likely to be full as empty; at the lowest temperature, the top of the filled states; in a semiconductor it can lie in the gap.
- **Forward and reverse bias.** A voltage across a junction that lowers its barrier (positive on the p side), and one that raises it.
- **Diode law.** $I = I_0(e^{eV/kT} - 1)$: the current through a junction grows as the Boltzmann factor of the forward voltage and settles at a small fixed value backward (Box 7.2).
- **Field-effect transistor; source; drain; gate; threshold.** A switch in which a voltage on a gate, through an insulating layer, draws a channel of carriers that joins two regions, the source and the drain; the gate voltage above which the channel forms is the threshold.

- **Integrated circuit.** Transistors, diodes and their connections made together in the surface of one chip of silicon.
- **Light-emitting diode (LED).** A junction of a direct-gap semiconductor that, with forward bias, gives out light whose photons carry about the energy of the gap.
- **Lumen.** The unit of light as the eye sees it; a lamp's efficiency is counted in lumens for each watt.
- **Photodiode; solar cell.** A junction that turns light into current, the light making electron-hole pairs that the junction's field carries apart; a solar cell is one made large to gather sunlight for power, turning at most about 30 percent of it into power with one junction.
- **Pixel.** The smallest point of an image; in a camera's sensor, one photodiode.

Part Three

Order Among Many



Chapter 8

Magnets

CHAPTER OVERVIEW

Iron holds a magnetic direction of its own, and copper holds none. An iron nail heated red-hot falls from a magnet. In this chapter I find why. Every electron is a small magnet, of one Bohr magneton, the natural unit of the electron's magnetism. An atom with a partly filled subshell carries a net magnetic moment, a measure of how strong a small magnet it is. Where such moments point every way, a field from outside lines them up only slightly, by a share that falls as one over the temperature (Curie's law, Box 8.1). Every material, copper among them, also answers a field weakly, in the direction against the field. Between neighboring atoms the electrons meet two rules at once. Electrons with aligned spins keep apart and push each other less, and a bond shared by two atoms takes two electrons of opposite spin. How far the atoms' states overlap, and how strongly the electrons push, decide which rule wins. So a crystal lines up every atom one way (a ferromagnet, such as iron), alternates them (an antiferromagnet), or leaves them unaligned (a paramagnet). The laws treat every direction alike, so an aligned crystal picks one direction and keeps it. Each atom's spin is held by its neighbors', and the direction is held by the whole crystal. The crystal picks among a few easy directions that spin-orbit coupling and the crystal's arrangement make equal: the cube edges in iron, the cube diagonals in nickel and the hexagonal axis in cobalt. Heat raises the entropy of unaligned arrangements, so alignment has the least free energy only below a definite temperature, the Curie

point, 1043 kelvin for iron. There the alignment is lost, at a point. In Box 8.2 I find that point by the mean field, which lets each spin feel its neighbors only through their average, and find above the point the Curie-Weiss law, Curie's law with the temperature counted from the Curie point. Slow twists of the held direction travel through the crystal as spin waves. A large magnet splits into domains, regions each aligned one way. It splits because its field outside costs energy that grows as its volume, while the walls between domains cost energy that grows only as their area, so large crystals divide and small grains keep one domain (Box 8.3, Figure 8.1). The moving of those walls gives a magnet its memory, and the lag of its magnetization behind a changing field, its hysteresis. The Higgs field shares the magnet's structure: laws alike in every direction, and a ground state that is not. It differs from the magnet in what can be found. Nothing can tell one of its picks from another, so it has no spin waves and no domains; and its mass lies far above the one below which its settling would jump, so it settled in a crossover, a smooth change with no sharp point.

I. Iron, Copper and a Red-Hot Nail

Chapter 7 ended with a question: some solids order not their atoms but their spins, so why does iron hold a direction? An electron's spin is the angular momentum it carries in itself, with no motion along a path, and with it the electron is a small magnet (Chapter 1, Section VI; Volume One, Chapter 8, Section II). Section II says more.

A small magnet picks up an iron nail, and it holds a note to the steel door of a refrigerator. A copper coin slides off it as if it were not there. Stroke a steel needle a few times along the magnet, always the same way, and hang the needle from a thread: it swings round until one end points north, and it goes on doing so for years. The needle has been given a direction, and it keeps it. Now hang an iron nail from the magnet and hold it in a hot flame. When the nail glows bright red it drops from the magnet, and when it has cooled the magnet draws it again.

So the reader's question is this: why is iron a magnet and copper not, and why does heat destroy a magnet?

Two results already in hand frame the answer. Volume One, Chapter 9, found that an atom with a partly filled subshell carries a net spin, and with it a magnetic moment. It does so because electrons whose spins point the same way keep apart, screen each other less and are held more strongly by the nucleus (Hund's first rule, Chapter 1, Section VII); iron, cobalt, nickel and gadolinium are such atoms. Chapter 2, Section XIV, found that a large collection of particles held at a fixed temperature settles where its free energy, its energy less its temperature times its entropy, $F = E - TS$, is least. Its entropy is the logarithm of the number of its microstates, its complete arrangements with every particle's state given, that share its totals (Chapter 2, Section III). So ordered arrangements, which usually have less energy and less entropy, win when it is cold. And Chapter 2, Section XV, found that such a change of order is sharp at a point where a symmetry separates the arrangements.

What is still needed is threefold: why the moments of iron's atoms line up with one another across a whole crystal while copper's atoms carry none to line up, why the direction they take is kept, and why heat takes it away. I find each in turn. Then I ask how the magnet's held direction compares with the settled value of the Higgs field. That value is the one other ground state in these two volumes and in *The Coming of the Kinds* that points one way while the laws do not, a ground state being a system's state of least energy (Chapter 1, Section VI). The comparison belongs to this book's question because the Higgs field's settled value gives the particles their masses, and so stands beneath every rung of the ladder (Chapter 1, Section II). A magnet is the nearest picture of it that a reader can hold in the hand, and the comparison shows how far that picture holds.

II. Every Atom a Small Magnet, or None

On a gusty day a field of weathervanes points every way at once, each vane knocked about by its own gusts. Let a light, steady breeze blow under the gusts, and on average the vanes lean a little downwind, more of them pointing with the breeze than against it. The stronger the gusts, the smaller the lean. How does a solid whose atoms are small magnets answer a magnet brought near it?

How strong a small magnet a body is, measured by the turning push that a magnetic field of a given strength gives it, is its *magnetic moment* (Chapter 1, Section VI). A coil carrying a current has one, and so does every electron. Angular momentum, the measure of turning motion (Chapter 1, Section IV), is kept because the laws of nature are the same in every direction. A charge going round makes a magnet, in proportion to its orbital angular momentum, the angular momentum of that motion. The electron's spin, its angular momentum in itself (Section I), carries a magnetic moment too. The natural unit of the electron's magnetic moment is the *Bohr magneton*, $e\hbar/(2m_e)$, the moment of one unit $\hbar$ of orbital angular momentum, with e the size of the electron's charge, $\hbar$ the reduced Planck constant and m_e the electron's mass. Its value is $9.2740100657 \times 10^{-24}$ joules for each tesla, among the values recommended in 2022 by the Committee on Data of the International Science Council (CODATA). Volume One, Chapter 8, Box 8.1, found that the electron's spin carries one whole Bohr magneton, though the spin is only half a unit. The reason is that the moment follows the whole turn of the spin's placement, the electron's relation to everything around it, which a particle of spin one half carries round with it as the belt's twist turns with the buckle (Chapter 1, Section V). The *tesla* is the unit of magnetic field, the field being the push and pull that moving charges and magnets exert on other moving charges

and magnets at each place around them. At the face of a strong permanent magnet the field is about one tesla, typically 1.3 tesla for a magnet of neodymium, iron and boron (standard tables of permanent magnets).

An atom's moment is the sum of its electrons'. In a filled subshell every state is taken twice, once with each direction of spin, and every orbital motion is matched by one in the opposite sense, so a filled subshell carries no moment at all. Only an atom with a partly filled subshell carries a net moment. Its unpaired spins, aligned by Hund's first rule (Volume One, Chapter 9, Section X), give it about one Bohr magneton for each unpaired electron.

In a solid, the question is what becomes of those moments. Copper's atom has a filled 3d subshell and one 4s electron beyond it, and in the metal that 4s electron joins the band of the shared electrons (Chapter 6). Each state of a band holds two electrons, one of each direction of spin (Chapter 6, Box 6.2), and the electrons fill the band's states in pairs from the bottom, so in copper metal the spins pair off and no atom carries a moment. In a *paramagnet*, by contrast, the atoms keep their moments, and nothing between the atoms lines them up: a salt whose metal ions have partly filled subshells is the plain case, its moments pointing every way like the weathervanes.

A field from outside gives each moment an energy that depends on how it points: lined up with the field it is lower, against the field higher (Volume One, Chapter 8, Section II). Heat knocks the moments about, as the gusts knock the vanes. How many point each way is set by the Boltzmann factor, $e^{-E/kT}$, the weight with which a small part of a large system at temperature T takes a state of energy E (Chapter 2, Box 2.3). I count them in Box 8.1.

Box 8.1. Curie's law from the Boltzmann factor

Premises. (1) Each moment in a paramagnet is one electron's spin, of moment μ_B, the Bohr magneton, read "mu B", and the spin is found along the direction of a field in one of two ways, with the field or against it (Volume

One, Chapter 1, Section V; Chapter 8, Box 8.1). (2) A moment μ_B in a field B has the energy $-\mu_B B$ pointing with the field and $+\mu_B B$ pointing against it (standard electromagnetism). (3) Each atom is a small part of a large system at temperature T, and it takes each of its two states with the weight $e^{-E/kT}$ (Chapter 2, Box 2.3); the moments do not act on one another. (4) For a small number x, the ratio $(e^x - e^{-x})/(e^x + e^{-x})$, written tanh x, is close to x (mathematics).

Steps. Write $x = \mu_B B/kT$. By (2) and (3), the weights of the two states are e^x and e^{-x}, so the average moment along the field is $\mu_B(e^x - e^{-x})/(e^x + e^{-x}) = \mu_B \tanh x$. At 1 tesla and 300 kelvin, $x = 9.274 \times 10^{-24}/(1.380649 \times 10^{-23} \times 300) = 0.0022$ (computed), so by (4) the average moment is $\mu_B x$: about two moments in a thousand more point with the field than against it. For n moments in each unit of volume, the moment of each unit of volume, the *magnetization*, is then $M = n\mu_B{}^2 B/(kT)$.

Result. A paramagnet's magnetization grows in proportion to the field and falls as one over the temperature, $M = C\,B/T$ with $C = n\mu_B{}^2/k$: *Curie's law* (Curie, 1895). At room temperature even a field of a tesla lines up only a few moments in a thousand, because μ_B times a tesla is the energy kT at about two thirds of a kelvin (computed).

So a paramagnet answers a magnet weakly, and less the warmer it is. It is drawn toward a magnet, and it keeps nothing when the magnet is taken away. Pierre Curie found the fall as one over the temperature by measuring many substances over a wide range of temperatures (Curie, 1895).

Every material, paramagnet or not, also answers a field in a second, weaker way. A field switched on near an atom changes the motion of all its electrons, the paired ones included. The change makes a small current in the atom whose own field opposes the field applied, as a current set going in a loop of wire by a magnet brought near opposes the magnet's field. So every material is pushed slightly away from a magnet: *diamagnetism*. Its size is measured by the material's *susceptibility*, the magnetization a field brings about for each unit of the field, written as a pure number. For cop-

per it is -9.63×10^{-6} and for water -9.035×10^{-6} at 20 degrees Celsius, the minus sign meaning that the material is pushed away (standard tables of magnetic susceptibilities). Small as it is, diamagnetism can hold up a living frog, which is mostly water, in the strong field inside a large magnet (Berry and Geim, 1997).

So we now know why copper is not a magnet. Its electrons are paired, in its filled 3d subshell and in its band, so none of its atoms carries a moment. It answers a magnet only by diamagnetism, and so it is pushed slightly away from the magnet instead of clinging to it. Iron's atoms carry moments, but so do a paramagnet's atoms, and theirs line up only in a field and only slightly, a few in a thousand at a tesla. A piece of iron lines up its moments with no field at all and holds them so up to 1043 kelvin. Something between the atoms must be lining them up, and it must be far stronger than any field from outside.

III. Aligned or Alternating

Volume One, Chapter 9, Section X, pictured two people carrying a long pole through a crowd, one at each end: nothing pushes them apart, and yet they are never found side by side, because the pole sees to it. Electrons whose spins point the same way are kept apart in that way, by a rule and not by a force. What happens to that rule when the electrons belong to two neighboring atoms of a crystal?

The lining up in iron comes from something far stronger than the atoms' magnets pulling on one another. Two moments of one Bohr magneton each, at the distance between neighboring atoms in iron, 0.248 nanometers, meet with a magnetic energy equal to kT at only 0.04 kelvin (computed; the distance from the side of iron's cubic cell, 286.65 picometers, standard tables of the elements). For the larger moment an iron atom carries in the metal, the energy equals kT at 0.2 kelvin (computed). Yet

iron holds its alignment up to 1043 kelvin. The lining up must come from something thousands of times stronger, and the electric push between electrons is the only force in the crystal of that strength.

Volume One, Chapter 9, Section X, found how the electric push can depend on the directions of spins. The state of two electrons changes sign when the two are exchanged (Chapter 1, Box 1.2). If their spins are aligned, the spin part of the state is the same after the exchange, so the part that says where they are must change sign. That part is therefore zero where the two would coincide, and the electrons keep apart, each surrounded by a region the other avoids, the *exchange hole*. Kept apart, they push each other less. Within one atom, the larger gain from keeping apart is that each electron screens the nucleus less from the other and is held more strongly by it (Volume One, Chapter 9, Section X). That gain is Hund's first rule. Between neighboring atoms whose partly filled subshells overlap, the keeping apart holds in the same way: electrons of the two atoms with aligned spins keep apart and push each other less, and that favors aligning the two atoms' spins.

A second rule pulls the other way. Two neighboring atoms can also share a pair of electrons in a bond, a covalent bond being a bond made by a pair of electrons shared between two atoms (Chapter 1, Section VIII). A shared state reaching over both atoms holds two electrons only if their spins are opposite, by exclusion, since two electrons of one spin in one state would be one electron (Chapter 1, Box 1.2). Sharing lowers the electrons' energy of motion, since a state that reaches over two atoms confines each electron less, and confinement costs energy (Volume One, Chapter 7, Section IV). So the sharing favors opposite spins on the two atoms.

Which rule wins is set by two quantities: how far the states of the neighboring atoms overlap, and how strongly the electrons push one another. Both are values that differ from one crystal to the next, set by the atoms and their spacing, and so the answer differs too. In a *ferromagnet* every atom's spin lines up the same way as its neighbors', and the moments add across the crystal. Iron, cobalt and nickel are ferromagnets at room temperature, and gadolinium below 293 kelvin (standard tables of

magnetic materials). In an *antiferromagnet* neighboring spins alternate, one way and then the other, in a fixed pattern, and the moments cancel across the crystal. And where the partly filled subshells of neighboring atoms hardly overlap, as in a salt whose magnetic ions stand far apart, neither rule acts with any strength. There the atoms' moments stay unaligned, and the crystal is a paramagnet (Section II).

Werner Heisenberg wrote the competition in one line (Heisenberg, 1928). The energy of two neighboring spins S_1 and S_2 is $-J\ S_1 \cdot S_2$. Here $S_1 \cdot S_2$ is the product of the spins' sizes and the cosine of the angle between them. The cosine of an angle is a number that tells how nearly two directions point the same way: it is 1 when they point the same way, 0 when they stand at right angles, and -1 when they point opposite ways. J, the *exchange constant*, is the energy that the keeping apart and the sharing together give to aligning the pair against opposing it. The energy of the crystal is the sum of such terms over every pair of neighbors. If J is positive, aligned neighbors have the lower energy, and the crystal is a ferromagnet when cold. If J is negative, opposed neighbors have the lower energy, and the crystal is an antiferromagnet. The name "exchange" comes from the change of sign on exchange that drives both rules. The energy depends only on the angle between the two spins, not on the direction either points in space: the exchange alone treats every direction alike. Section IV returns to this sameness.

In iron, cobalt and nickel the moments belong to d electrons that are not wholly held at their own atoms. The 3d states of neighboring atoms overlap enough to make a band (Chapter 6, Section III), and the band is narrow in energy. Chapter 6, Section III, found that a band is wider the more the states of neighbors overlap. The d states of neighbors overlap only a little, so the d band spans a smaller range of energy than the band of the outer s electrons. Edmund Stoner found the rule for when such a band aligns (Stoner, 1938). Aligning some of the band's spins costs energy of motion, because electrons must move up into empty states of the aligned direction. It saves energy of push, because aligned electrons keep

apart. Stoner wrote the push as an energy I, the energy by which the push between two electrons on one atom is lessened when their spins are aligned. The density of states is the number of states in each small range of energy near a given energy (Chapter 6, Section IV). Stoner wrote it at the Fermi level for each atom and each direction of spin, as a number of states for each unit of energy. The product of the energy I and the density of states is then a pure number, and the saving wins when that number passes one. A narrow band has many states in each range of energy, and a partly filled narrow band has many of them at the Fermi level, so iron's, cobalt's and nickel's d bands pass the rule. Copper's d band is full and lies below the Fermi level, so copper has no partly filled band of that kind to align. Because the d electrons are shared through a band, an atom in the metal carries a moment that is not a whole number of Bohr magnetons: 2.22 in iron, 1.72 in cobalt and 0.606 in nickel (Kittel, 1996). The fractions are the mark of a band: a moment held wholly at one atom would come in whole Bohr magnetons, and iron's 2.22 is the moment Box 8.2 uses.

Neutrons find what a magnet cannot: the alternating spins of an antiferromagnet, whose moments cancel and so give a magnet nothing to pull on. A neutron carries a magnetic moment (Volume One, Chapter 3, Section VII), so neutrons scattered by a crystal answer to the directions of its atoms' moments as well as to the places of its atoms. Clifford Shull and J. Samuel Smart sent neutrons through manganese oxide and found, below 116 kelvin, scattering that needed a repeat twice the repeat of the atoms themselves (Shull and Smart, 1949). The spins of the manganese ions alternate, so the pattern of spins repeats only every second atom. The spins' repeat at every second atom is the doubling of the repeat of Chapter 6, Section V. In Chapter 6, Section V, I named the doubling as one way that a crystal with an odd count of electrons in each cell can change on cooling: the alternating order of spins doubles the count in each cell. The temperature below which an antiferromagnet's spins alternate is its *Néel temperature*, after Louis Néel, who described the alternating order in 1932 (Nobel

Foundation, 1970). It is 116 kelvin for manganese oxide, 525 kelvin for nickel oxide and 308 kelvin for chromium, which is an antiferromagnetic metal (standard tables of magnetic materials).

A third pattern lies between aligned and alternating spins. Where the alternating moments are of unequal size, because the two sets of sites hold different ions or different numbers of them, the moments do not cancel. The crystal then has a net moment, as a ferromagnet does: it is a *ferrimagnet* (Néel, 1948). Lodestone, the stone through which magnetism was first found in antiquity, is a ferrimagnet (du Trémolet de Lacheisserie, Gignoux and Schlenker, 2005). It is magnetite, an oxide of iron in which the ions on two kinds of site point opposite ways, and it holds its order up to 858 kelvin (standard tables of magnetic materials). The ceramic magnets of loudspeakers and refrigerator doors, the hard ferrites, are ferrimagnets too: oxides of iron with barium or strontium, in which unequal moments on two sets of sites point opposite ways (Smit and Wijn, 1959).

So we now know why some crystals line up their spins and others alternate them. Electrons with aligned spins keep apart and push each other less, between neighboring atoms as within one atom. A bond shared between neighbors takes two electrons of opposite spin. The overlap of the atoms' states and the strength of the push, which are values set by each crystal, decide which rule wins. So a crystal of atoms with partly filled subshells may align every atom one way, alternate them in a fixed pattern, or leave them unaligned. Iron aligns, because its d band is narrow and partly filled. Copper has nothing to align.

IV. One Direction, Held by the Whole Crystal

Guests sit down at a round dinner table set with one napkin between each two places, so that every guest has a napkin on the left and one on the right, and no rule says which is whose. The table is the same whichever way round one goes. Then one guest takes up the napkin on the right, and the neighbor, whose left-hand napkin is now gone, must take the one on

the right as well, and so on round the table, until every guest has taken a right-hand napkin. Nothing in the table chose right over left. The choice was made once, and every guest's choice is held by the neighbors'. How does an aligned crystal come to point one way, when the laws it obeys favor no direction?

The laws of nature are the same in every direction, and that sameness is why angular momentum is kept (Section II). The exchange energy of Section III, $-J\ S_1 \cdot S_2$, keeps that sameness: it depends only on the angles between neighboring spins, so turning every spin of a ferromagnet together through any angle, about any axis, leaves its energy as it was. Yet the ferromagnet's state of least energy has every spin pointing one way, along some one direction, and so it is not the same in every direction. A ground state that is not the same in every direction, under laws that are, is the plain mark of *spontaneous symmetry breaking*: a symmetry of the laws that the state of least energy does not share. There are as many such ground states as there are directions, all of equal energy, and the crystal is found in one of them.

So an aligned crystal picks one direction, and it holds that direction. Each atom's spin is held where it points by its neighbors' spins, since turning it alone would set it against all of them at the cost J for each neighbor. Those neighbors are held by theirs, so the direction is held by the whole crystal, as the right-hand napkins are held by the whole table.

The direction is a record. An outcome is a record when it is held by something that keeps it, something large enough that the outcome is not undone by the small jostlings of its parts. A compass needle set beside the crystal swings to the crystal's direction, and a second needle set beside it later swings the same way: the direction is found, and found again. What holds it is the crystal, about 8.5×10^{22} atoms in each cubic centimeter of iron, each held by its neighbors (computed from iron's density, 7.874 grams for each cubic centimeter, and its atomic weight, 55.845, standard tables of the elements). And what is held is kept. The held direction is a direction of angular momentum, since each aligned moment belongs to a

spin, and angular momentum is kept. So the direction of the whole crystal's spin can be changed only by something outside that gives or takes angular momentum. Albert Einstein and Wander de Haas showed that the magnetization is angular momentum in this way (Einstein and de Haas, 1915). An iron rod hung from a thread and magnetized along its length by a coil turns slightly about its length, because the angular momentum the spins take up in lining up must be given up by the rod as a whole. *Measurement*, Chapter 12, Section VII, states what such a record is: "A record is itself an irreversible change, a darkened grain of emulsion or a registered count, and making it raises the entropy of the instrument that holds it". Setting a magnet's direction is a change of that kind. As a piece of iron is set into one direction, its regions of one alignment grow in small jumps, each caught and then released by flaws in the metal (Section VII). Each jump turns part of the energy into heat, which raises the entropy of the iron and its surroundings. Nothing inside the crystal turns the direction back: only a field from outside, doing work on it, can set it another way (Section VII). A magnet's direction is a record made by an irreversible change, and it is the ground of a magnet's memory, which Section VII and the hard drives of In Use put to work.

Are all directions alike inside a crystal that can be turned onto itself only by certain parts of a turn? They are not, and the reason changes what the crystal picks among. The exchange of Section III treats every direction alike, but a second, smaller energy does not. *Spin-orbit coupling*, the meeting of an electron's spin magnet with the magnetic field it finds, in its own frame, from its motion through the electric field around it (Volume One, Chapter 8, Section III), ties each electron's spin to its orbital motion. That orbital motion is shaped by the crystal's arrangement, since each d electron's state is pushed by the charges of the neighboring atoms, which sit along the crystal's own axes. So the energy of the aligned crystal depends, slightly, on which way its alignment points relative to the crystal's axes. This dependence is *magnetocrystalline anisotropy*, and the directions of lowest energy are the crystal's *easy axes*. Spin-orbit coupling is the chief source of the anisotropy (standard physics of magnets).

For a crystal of cubic symmetry, write the direction of the alignment by its three cosines α_1, α_2, α_3, read "alpha one, alpha two, alpha three", one for the angle it makes with each of the three cube edges (Section III gave the cosine). The squares of the three cosines always add to one, so an energy built from those squares alone is the same in every direction. The simplest energy that differs from one direction to another, of those the cube's symmetry allows, is therefore built from products of the squares, two at a time. For each unit of volume it is $K_1(\alpha_1^2\alpha_2^2 + \alpha_2^2\alpha_3^2 + \alpha_3^2\alpha_1^2)$, with K_1 a constant of the material (standard physics of magnets). Along a cube edge, one cosine is 1 and the others 0, and the bracket is 0. Along a cube diagonal, every cosine squared is 1/3, and the bracket is 1/3, its largest value. So where K_1 is positive the edges are easy, and where it is negative the diagonals are. For iron K_1 is 4.8×10^4 joules for each cubic meter and for nickel -0.5×10^4, at room temperature (standard tables of magnetic materials). So iron's easy axes lie along the cube edges, six directions, and nickel's along the cube diagonals, eight directions. Cobalt's crystal is hexagonal, and the simplest such energy for each unit of volume is $K_1 \sin^2\theta$, with θ, read "theta", the angle from the hexagonal axis. The sine of that angle, $\sin\theta$, is 0 along the axis and 1 at right angles to it, and $K_1 = 45 \times 10^4$ joules for each cubic meter (the same source). So cobalt's easy axis is its hexagonal axis, two directions.

The easy directions come in pairs, each with its reverse, for a reason deeper than the crystal. Reversing every motion in the crystal reverses every spin and every orbital motion together, and the laws are the same under that reversal of time, so the energy of an alignment and of its reverse are equal. So the aligned crystal picks among a finite set of equal directions, the easy directions that the crystal's symmetry and the reversal of time make equal: six for iron, eight for nickel, two for cobalt. It is still a pick made once and held by the whole, as the napkins were: only now the table offers a few equal napkins in place of every direction there is. The anisotropy also makes the held direction harder still to turn. Turning the whole alignment of a region from one easy direction to the next must now

pass over the harder directions between them, at a cost that is the anisotropy energy for each unit of volume times the volume turned. The weight with which heat makes such a change is the Boltzmann factor of an energy that grows with the number of atoms turned (Chapter 2, Section X). For any region of ordinary size that weight is far too small for the change to happen in any time that could be waited. Only grains so small that the barrier is a few times kT lose their direction to heat.

So we now know how a crystal comes to point one way. The laws, and the exchange that aligns the spins, treat every direction alike, yet the crystal's state of least energy points one way. The crystal picks one of its equal easy directions, set by spin-orbit coupling and its own arrangement, and holds it, each spin held by its neighbors and the direction held by the whole. The direction is a record: it is found against a compass and found again, and what holds it, the whole crystal, keeps it.

V. Heat Takes the Alignment Away

The iron nail of Section I dropped from the magnet when it glowed bright red, and the magnet drew it again when it had cooled. Iron at 770 degrees Celsius is no longer a magnet at all, though every one of its atoms still carries its moment. Why does heat take the alignment away, and why at one temperature?

The free energy decides, as Chapter 2, Section XIV, found for every change between order and disorder. Aligned, a ferromagnet has the lower energy, by the exchange of every pair of neighbors. Unaligned, it has far the larger entropy: each spin one half is free to point either way along an axis, two choices for each atom, so a crystal of N atoms has 2^N unaligned arrangements against one aligned arrangement for each easy direction. Entropy is the logarithm of the number of a system's microstates with its totals (Section I). So the unaligned crystal's entropy is larger by about N k ln 2, with ln the natural logarithm, the logarithm to the base e = 2.718 (Chapter 2, Section III). The free energy F = E − TS weighs the two. When

the crystal is cold, the energy rules and alignment wins; when it is hot enough, the term TS rules and the unaligned arrangements win. So the alignment is held only below a definite temperature, and above it the crystal is a paramagnet.

The change does not run evenly from one arrangement to the other as the temperature rises. Each spin is lined up by the exchange with its neighbors, and how strongly the neighbors line it up depends on how well they are lined up themselves. So as heat loosens the alignment, it loosens what holds the alignment, and the loosening feeds on itself. Pierre Weiss followed that feeding with one idea: let each spin feel its neighbors only through their average, as if their exchange were a field in proportion to the crystal's magnetization (Weiss, 1907). Weiss's one idea is the *mean field*, and in Box 8.2 I follow the mean field to the point where the alignment is lost.

Box 8.2. The mean field and the Curie-Weiss law

Premises. (1) A moment μ_B of spin one half in a field B at temperature T has on average the moment $\mu_B \tanh(\mu_B B/kT)$ along the field (Box 8.1). (2) The mean field: each spin feels the exchange with its neighbors as if it were a field $B_m = b\,m$ along the alignment, where m, from -1 to 1, is the share of the full alignment that the crystal has, the magnetization over its largest value, and b is set by the exchange constant J and the number of neighbors; the jostling of the neighbors about their average is set aside, and that setting aside is what defines the mean field (Weiss, 1907). (3) For a small number x, $\tanh x = x - x^3/3$ to the next order (mathematics). (4) Where the equation for m found below has a solution with m different from zero below the point found, that solution has the lower free energy (standard physics of the mean field).

Steps. By (1) and (2), with an outside field B, each spin's average share is $m = \tanh(\mu_B(B + bm)/kT)$, and the same m must come out as went in. Write $T_C = \mu_B b/k$. With no outside field, $m = \tanh(mT_C/T)$. The right side starts from zero with the slope T_C/T and bends down as m grows. If

T is above T_C, the slope is less than one, and the right side lies below the line m for every positive m: the only solution is m = 0, no alignment. If T is below T_C, the slope is more than one, and the right side crosses the line m at a value m_0 different from zero, and at $-m_0$; by (4) the crystal is aligned. Just below T_C, m is small, and by (3), $m = mT_C/T - (mT_C/T)^3/3$, so to lowest order $m^2 = 3(T_C - T)/T_C$: the alignment grows from zero as the square root of the distance below T_C. Above T_C, with a small outside field, $m = \mu_B B/kT + (T_C/T)m$ to lowest order, so $m = \mu_B B/(k(T - T_C))$, and for n spins in each unit of volume the magnetization is $n\mu_B m = C\,B/(T - T_C)$, with the C of Box 8.1.

Result. A ferromagnet is aligned with no outside field below the temperature $T_C = \mu_B b/k$, and not above it; its alignment grows from zero at T_C, with no jump. Above T_C it is a paramagnet whose magnetization is $C\,B/(T - T_C)$: the *Curie-Weiss law*, Curie's law with the temperature counted from T_C. For iron, T_C = 1043 kelvin gives $b = kT_C/\mu_B$ = 1,550 tesla for spins of one Bohr magneton (computed), or about 700 tesla for iron's moment of 2.22 Bohr magnetons: the neighbors hold each spin as a field of about a thousand tesla would, hundreds of times the field of the strongest permanent magnet.

The field of a thousand tesla is the exchange of Section III, the electric push between electrons sorted by their spins, written as if it were a magnetic field. It is why iron holds its alignment to a bright red heat, and it is far beyond anything the atoms' magnets could do to one another.

The temperature at which the alignment is lost is the Curie point. The *Curie point* is the temperature at which a magnet loses its alignment, at a point because a symmetry separates the arrangements (Chapter 2, Section XV). Below it, the spins pick one direction from among the equal ones. Above it, no direction is picked. And no arrangement lies between picking a direction and not picking one. The Curie point is 1043 kelvin for iron, 1400 kelvin for cobalt, 627 kelvin for nickel and 293.2 kelvin for gadolinium (standard tables of magnetic materials). The loss at the Curie point is

a *continuous change*, a change in which the order grows from nothing at one point, with no jump and no latent heat (Chapter 4, Section V). The magnetization of iron falls toward zero as the Curie point is approached from below, and it is zero above it, with no heat taken in at the point itself.

The mean field finds the Curie point and the kind of change that happens there, a continuous one. Close to the point, the alignment grows as a power of the distance below it, $(T_C - T)^{\beta}$, read "beta", and there the measured power is set by what the mean field leaves out. The mean field gives $\beta = 1/2$ (Box 8.2), because it lets each spin feel only the average of its neighbors. Near the point the crystal's fluctuations, the small, ever-changing differences of its macrostate from the most probable one, which the motion of its particles makes (Chapter 2, Section IV), reach over large regions, and those are just what the mean field sets aside. Counted in full, they give a smaller power, which is the one measured. The powers that describe a change of order close to its point are its *critical exponents*. They depend only on the number of dimensions and on the kind of thing that orders, and not on the material: this is *universality*. For an order whose direction can point any way in three dimensions, as iron's nearly can, $\beta = 0.3689$. For an order along one axis only, $\beta = 0.326$, and the same exponent describes the liquid and gas of Chapter 4 near their critical point (standard tables of critical exponents). Universality is why heat takes the alignment away in one way from every magnet of a kind near its Curie point: how the alignment vanishes there does not depend on iron's own values, only on the dimension and on what orders. Every order whose direction can point any way in three dimensions is lost with one power, and every order along one axis, the difference between a liquid and its gas among them, with another.

So we now know why heat destroys a magnet. Heat raises the entropy of the unaligned arrangements, so the free energy is least for alignment only below the Curie point. Since each spin's alignment is held by its neighbors' alignment, the alignment falls away faster and faster as the Curie point is approached. It is lost there, at a point, because no arrange-

ment lies between a picked direction and none. For iron the Curie point is 1043 kelvin, 770 degrees Celsius, the bright red heat at which the nail dropped.

VI. Slow Twists of the Held Direction

Wind blowing over a field of ripe wheat bends each stalk a little and lets it spring back, and a wave of bending runs across the field, though no stalk leaves its place. The stalks all stand one way, and the wave is a slow twist of that one way, passed from stalk to stalk. What happens when the held direction of a magnet is twisted a little, from place to place?

Section IV found that turning every spin of a ferromagnet together costs no exchange energy, since the exchange depends only on the angles between neighbors. Turning the spins by slightly different amounts from place to place costs a little, because neighbors then stand at a small angle to one another, and the cost is smaller the more slowly the twist changes along the crystal. So a twist of the held direction that varies over a long distance costs very little energy, and a twist that varies over a short distance costs more. Such a twist does not stay put. Each tilted spin turns about the direction its neighbors hold, as a tilted top turns about the upright, and the tilt passes from spin to spin along the crystal as a wave: a *spin wave*, which Felix Bloch found in 1930 (Bloch, 1930).

Spin waves come in quanta, as the vibrations of a lattice do, and the quanta are called *magnons*. A magnon, like a phonon, is a *collective excitation*, a motion shared by many particles at once that comes in quanta (Chapter 5, Section IV), and it is not a kind of particle. In a ferromagnet the energy of a magnon grows as one over the square of its wavelength, so the longest waves cost least of all (Bloch, 1930). The small anisotropy of Section IV gives even the longest a small least energy. Neutrons scattered from a magnet give up or take up the energy of single magnons, and the energies of spin waves of each wavelength are measured in that way (standard physics of magnets).

Spin waves are the magnet's form of a general result. Where a symmetry of the laws is hidden in the ground state, moving along the direction of the hidden symmetry costs no energy. A wave of such motion then costs an energy that falls toward zero as the wave is made longer, and its quantum is called a *Goldstone boson*. Among the particles a Goldstone boson is a massless whole of spin zero, as the pions nearly are (Volume One, Chapter 2, Section VIII). In a magnet it is a collective excitation that carries one unit ħ of spin. In a magnet the hidden symmetry is the sameness of all directions, and the motion along it is the turning of the held direction. The waves of that motion are spin waves, and their quanta, being motions of the spins of a solid's atoms, are collective excitations. In a real crystal the anisotropy of Section IV tips the sameness slightly, which is why even the longest spin wave keeps the small least energy found above. Spin waves are what a findable direction does when it is twisted slowly: the direction can be twisted because it can be found, place by place, against the directions held nearby. Section VIII returns to this link between a direction that can be found and the waves that twist it.

Spin waves also carry the first loss of alignment as a magnet warms from the coldest temperatures. Each magnon lowers the crystal's total spin by one unit ħ, and heat makes more of them the warmer the crystal is. So a ferromagnet's magnetization falls slightly below its largest value even far below the Curie point, as the temperature to the power three halves (Bloch, 1930).

So we now know what a slow twist of a magnet's held direction does. It costs an energy that falls toward zero as the twist is made slower, and it runs through the crystal as a spin wave. The spin wave's quanta, magnons, are collective excitations, and they are the Goldstone bosons of the magnet's hidden symmetry.

VII. Domains, and a Magnet's Memory

An iron nail from a box of nails lies beside a paper clip and does not pick it up, though every atom of its iron is aligned with its neighbors at room temperature, far below the Curie point. Stroke the nail with a magnet, and it picks up the clip. In 1919 Heinrich Barkhausen wound a coil round a bar of iron, joined the coil to a telephone receiver, and brought a magnet slowly near the bar: the receiver crackled, a click at a time, though the magnet moved smoothly (Barkhausen, 1919). If iron's spins are aligned, why is an ordinary piece of iron not a magnet, and what do the clicks hear?

An aligned crystal has a magnetic field of its own. The field runs out of one end of the crystal, round through the space outside it, and back in at the other end, and it fills the crystal's inside as well. A magnetic field carries energy, $B^2/(2\mu_0)$ in each unit of volume, with B the field (standard electromagnetism). Here μ_0, read "mu nought", is the magnetic constant, the constant that fixes, in the international units, how strong a field a given current makes: $1.25663706127 \times 10^{-6}$ newtons for each ampere squared (CODATA 2022). That energy is a cost the crystal pays for being aligned all one way, and the larger the crystal, the larger the space its field fills and the larger the cost.

The crystal can lessen the cost by breaking its alignment into regions aligned in different directions. A *domain* is a region of a magnet within which every spin points one way, along one of the easy directions of Section IV. Neighboring domains magnetized in opposite or crossing directions have fields that partly cancel one another outside, so the field outside, and the energy it carries, is smaller than a single domain's (Figure 8.1). Pierre Weiss proposed that a ferromagnet is divided in this way in the same work in which he proposed the mean field (Weiss, 1907), and that is why an ordinary nail picks up nothing: its domains point every way, and their fields cancel.

Breaking into domains has a cost of its own. Between two domains lies a *domain wall*, the thin layer in which the spins turn from one domain's direction to the other's. Turning sharply, from one atom to the next, would set neighbors at a large angle and cost much exchange energy. Turning slowly, over many atoms, keeps the angles small but holds many spins along the harder directions between the easy ones, and that costs anisotropy energy. The wall settles between the two, with the spins turning over some hundred to a hundred and fifty atoms (standard accounts of magnetic domains), and it costs an energy σ, read "sigma", for each unit of its area. So the question is whether the walls cost less than the field saves, and I answer it in Box 8.3.

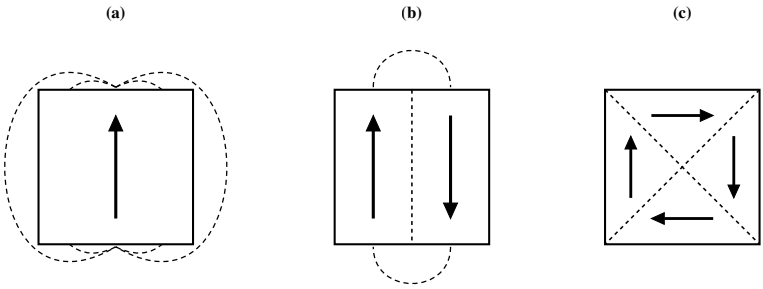
Box 8.3. Domains from area against volume

Premises. (1) A grain of a ferromagnet of size L, a length across it, magnetized as one domain with the magnetization M_s of full alignment, carries in its field an energy $c\mu_0 M_s^2 L^3$, where c is a pure number set by the grain's shape; for a sphere the field's energy is $\mu_0 M_s^2 V/6$, with V its volume (standard electromagnetism). (2) Dividing the grain by a wall into two domains magnetized in opposite directions, as in Figure 8.1 (b), lessens the field's energy by a fraction f of its single-domain value, with f a pure number of order one half, set by the shape; adding domains that close the field inside the grain, as in Figure 8.1 (c), removes nearly all of it (standard electromagnetism). (3) A wall costs an energy σ for each unit of its area, set by the exchange and the anisotropy and independent of the size of the grain (this section).

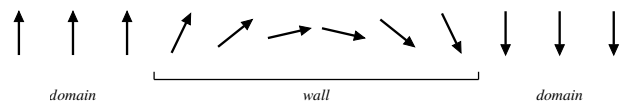
Steps. One domain: the field costs $c\mu_0 M_s^2 L^3$, by (1). Two domains: a wall across the grain has an area of about L^2, and costs about σL^2, by (3), while the field's cost falls by $fc\mu_0 M_s^2 L^3$, by (2). Dividing pays when $fc\mu_0 M_s^2 L^3$ is greater than σL^2, that is, when L is greater than $L_c = \sigma/(fc\mu_0 M_s^2)$. The saving grows as L^3, the volume, and the cost as L^2, the area, so for every grain larger than L_c dividing pays, and it pays more the larger the grain; for every grain smaller than L_c a single domain has the lower energy. In a

large crystal divided into many slabs of width D, the walls cost σ for each unit of area of each of L/D walls, and the field left near the surfaces reaches about D into the space outside, so its cost goes as $\mu_0 M_s^2 D$ for each unit of surface; the sum of the two is least where D grows as the square root of $L\sigma/(\mu_0 M_s^2)$.

Result. A large ferromagnet divides into domains, because the energy of its field outside grows as its volume while the energy of the walls between domains grows only as their area; the larger the crystal, the more domains it pays to make, and their width grows as the square root of the crystal's size. Below a size of order $\sigma/(\mu_0 M_s^2)$, times a number set by the shape, a grain keeps one domain. Measured single-domain grains of most ferromagnets are between about 25 and 80 nanometers across, and the domains of a large crystal are commonly a micrometer to a tenth of a millimeter across (standard accounts of magnetic domains), large enough to be seen under a microscope in light reflected from a polished surface.



(d) inside a wall the spins turn little by little, over many atoms



sketch, not to scale

Figure 8.1. Domains in a magnet, drawn as a sketch and not to scale. (a) A grain magnetized as one domain (arrow) sends a large field round through the space outside it (dashed lines). (b) Divided by one wall (dotted) into two domains magnetized in opposite directions, it sends a smaller field outside, which loops from one domain to the other near the ends. (c) With domains along its edges that close the field inside it, the four domains magnetized round a loop, it sends almost no field outside, at the cost of four walls. (d) Inside a wall the spins turn from one domain's direction to the other's a little at each atom, over many atoms. The energy the field saves grows as the volume of the grain and the energy the walls cost grows as their area (Box 8.3), so large crystals divide and small grains keep one domain.

So a large piece of iron is a patchwork of domains, and the magnetizing of a nail is the rearranging of the patchwork. A field from outside favors the domains whose direction lies nearest its own. At first the walls move, so that the favored domains grow at the expense of their neighbors. In a stronger field the domains that remain turn their direction toward the field's. At last the whole nail is one domain, or nearly, magnetized along the field. The walls move in jumps: they catch on flaws, on stray atoms and at the boundaries of the grains of the metal (Chapter 5, Section VI), and they break free one jump at a time. Each jump sets a small current going in a coil round the iron. Those jumps are Barkhausen's clicks.

Take the field away, and the walls do not all go back, since the flaws that caught them on the way still hold them, and the nail stays magnetized: the magnetization it keeps with no field is its *remanence*. To bring the magnetization back to zero, a field must be applied the other way, and the field needed is the magnet's *coercivity*. Traced against the field applied, as the field is swept up and down, the magnetization runs round a loop, lagging behind the field, and does not return along the path it came by. That lag, which makes a magnet's magnetization depend on the history of the field and not only on the field now, is *hysteresis*, and the loop is the magnet's loop of hysteresis. The area inside the loop is the energy that each sweep up and down turns into heat in the magnet.

The width of the loop sorts magnets into two families. A *soft magnet*, such as iron with a little silicon in it, has walls that move easily, a small coercivity and a narrow loop: it magnetizes in a weak field, gives up its magnetization when the field goes, and loses little energy in each sweep. A *hard magnet* has a large coercivity and a wide loop: once magnetized, it keeps its magnetization against fields that would undo a soft one. The strongest hard magnets are made of neodymium, iron and boron, in a crystal, $Nd_2Fe_{14}B$, with a single easy axis and a very large anisotropy (Sagawa, Fujimura, Togawa, Yamamoto and Matsuura, 1984; Croat, Herbst, Lee and Pinkerton, 1984). A powder of its grains is lined up in a field, pressed, heated until the grains join, and then magnetized once in a strong field. Its grains are near the single-domain size of Box 8.3 and their easy axes lie together, so few walls can form and those that do are held. The magnet keeps a remanence of typically 1.3 tesla (standard tables of permanent magnets).

Heat undoes a magnet's memory by the same steps that made it. Warmed, the walls are shaken loose from the flaws that held them, and the domains rearrange toward the state of least energy, in which their fields cancel. Above the Curie point the alignment within each domain is lost too, so that when the iron cools again it divides into domains pointing every way. So the nail of Section I, red-hot and then cooled, is no longer a magnet. A magnet of neodymium, iron and boron loses its order above about 583 to 673 kelvin, its Curie point (standard tables of permanent magnets).

So we now know why a piece of iron is a magnet only when it has been made one. Its own field costs energy that grows as its volume, and the walls between domains cost energy that grows only as their area. So a large crystal divides into domains whose fields cancel, while a grain smaller than a few tens of nanometers keeps one domain. A field from outside moves the walls and turns the domains, the walls catch on flaws, and what they keep when the field is gone is the magnet's memory: its remanence, its coercivity and its loop of hysteresis.

VIII. A Magnet and the Higgs Field

A town has one clock in its tower, and every clock and watch in the town is set by it each morning. Nothing outside the town keeps time. A stranger may say that the tower clock is an hour fast. But turn the tower's hands an hour on, and every clock in the town follows it the next morning, and no comparison made inside the town can show that anything has changed: every reading of the time is taken from the tower. A compass needle is not like that tower. Its direction can be compared with the walls of the room, the stars and a second compass. The Higgs field settled into a value that points one way, as a magnet's spins do. Is its direction a magnet's direction, or the tower's?

The magnet and the Higgs field share one structure, and it comes first. The Higgs boson is the particle of the Higgs field, a field present everywhere in space whose settled value gives the W and Z, the quarks and the charged leptons their masses (Chapter 1, Section II). The weak force turns one kind of quark or lepton into another (Chapter 1, Section II). A *doublet* is a pair of kinds that the weak force turns into each other, such as the up and down quarks, or the electron and its neutrino. At each point the Higgs field has two components, one for each side of a doublet (*The Coming of the Kinds*, Chapter 6, Section III). The laws of the weak force are the same under every rotation of the two components into each other, as the laws of a magnet are the same under every turning of its spins. And the field's settled value, like the magnet's alignment, is not the same under those rotations. *The Story of the Particles*, Level 8, Section III, states it in one line: "The vacuum itself picks one direction in the doublet space: a ground state that is not symmetric even though the underlying laws are". So the Higgs field's settled value has the structure that Section IV called spontaneous symmetry breaking: a symmetry of the laws that the state of least energy does not share. Both came about as order wins when cold. The magnet's alignment came below its Curie point. The Higgs field's value came

as the early universe cooled through about 160 GeV, the energy, written as kT, at which the carriers of the weak force took their masses (*The Coming of the Kinds*, Chapter 6). Laws alike in every direction, and a ground state that is not: that is the structure the magnet and the Higgs field share.

They differ in what can be found. A magnet's direction can be found against other things. A compass finds it. The crystal's own axes find it, since the direction lies along an easy axis that the crystal's arrangement fixes (Section IV). Two domains find it in each other, since each is aligned differently from its neighbor (Section VII). Because it can be found place by place, it can be twisted from place to place, and its slow twists run through the crystal as spin waves (Section VI). It splits into domains. And it is lost at a sharp Curie point, because no arrangement lies between a picked direction, which can be found, and none (Section V).

The Higgs field's direction in its doublet space is the tower clock. Every label by which a direction in that space could be found is read from the field's own settled value. One such label is which side of a doublet carries electric charge. Another is which carrier is the photon. The joined force of the weak force and electromagnetism has four carriers, and the photon and the Z boson are each a combination, a mixture, of two of them (*The Coming of the Kinds*, Chapter 6, Section III). A carrier "reads" the settled value, in that book's word, when turning the states it acts on would change the value. The Coming of the Kinds puts it so: "One of the two combinations reads nothing in the settled value, because the field's value sits on the side of the doublet that carries no electric charge" (Chapter 6, Section III). That combination is the photon. So whatever direction the field picks, the side it sits on is, by that very pick, the side that carries no charge. Turn the pick, and every label turns with it, and no comparison shows anything changed. Nothing can tell one such pick from another. A direction of this kind, which the labels it defines carry along with it, is what physicists call a direction of gauge symmetry, a symmetry whose rotations can be made separately at every place. The tower clock shows in a picture that a pick of such a symmetry cannot be found, and Shimon Elitzur proved it for every symmetry of this kind: no

measurement finds its pick, as a compass finds a magnet's (Elitzur, 1975). So the Higgs field's settled value has the structure of Section IV, laws that share a symmetry the settled value does not, without the magnet's findable pick.

Three consequences follow, each the reverse of a magnet's. First, the Higgs field has no spin waves. At each point each of its two components carries a size and a phase, the phase being the stage of a wave's swing counted as a fraction of a whole turn (Chapter 6, Section II). So the field has four states at each point (*The Coming of the Kinds*, Chapter 3, Section IV). In a magnet a slow twist of the direction from place to place is a wave of its own, the spin wave. In the Higgs field a twist of the pick from place to place turns the labels with it, and the states that would carry such twists are taken up by the carriers. A carrier with no mass turns in two ways about its line of motion. A carrier with mass has a third way of turning, along its line of motion (*The Coming of the Kinds*, Chapter 6, Chapter Overview). That book states where the four states go: "Of the field's four states, three become the third states of turning of the W^+, W^- and Z, and the fourth remains as the Higgs boson" (the same place). Second, the Higgs field has no domains, since two regions of the field have no difference of pick that any comparison could show. Third, it has no sharp point. Chapter 2, Section XV, found that a change of order is sharp at a point, in the limit of many particles, only where a symmetry or a jump separates the arrangements. For the magnet the symmetry separates them, because a picked direction can be found and the lack of a pick can be found too. For the Higgs field no comparison shows the pick, so the symmetry cannot separate the settled field from the unsettled one. A sharp point could then come only from a jump, a sudden change of the field's value at one temperature. In a jump, bubbles of the settled field would grow in the unsettled one, as bubbles of steam grow in boiling water (*The Coming of the Kinds*, Chapter 4, Section IV). Whether there is a jump is set by the Higgs boson's mass. The mass measures how stiffly the field's value is held at its settled size. A light Higgs boson goes with a soft field, which the carriers' share of the energy can tip into a jump; a heavy one goes with a stiff field,

which changes smoothly (standard physics of the settling of the Higgs field). The Standard Model is the full theory of the kinds and their forces. Computations of it, made on a grid of points that stands in for space and time, show that the jump shrinks to nothing at an endpoint, a Higgs mass near 72 GeV (*The Coming of the Kinds*, Chapter 4, Section IV). Below the endpoint the settling would jump, and above it no jump is left. The measured mass is 125.13 ± 0.11 GeV, far above the endpoint. So the Higgs field settled with no point at all: "The field takes its value smoothly, in a crossover with no jump" (*The Coming of the Kinds*, Chapter 6, Chapter Overview), a crossover being a smooth change between arrangements with no jump and no point (Chapter 2, Section XV). The magnet's sharp Curie point belongs to the magnet's findable direction, and the Higgs field, with no findable direction, settled smoothly.

Is there a state of matter that matches the Higgs field more closely than a magnet does? There is, and it is the one in which the Higgs field's rule for giving a carrier its mass works again, inside a solid. *The Coming of the Kinds*, Chapter 6, Section III, states the rule: "A carrier becomes massive when the settled value of the field tells apart the states it rotates among". In a metal cooled into the state of Chapter 9, a magnetic field reaches only a thin layer at the surface, as the field of a carrier with mass reaches only a short way. In Chapter 9 I find why.

So we now know how a magnet's held direction stands beside the Higgs field's settled value. Both have laws alike in every direction and a ground state that is not. The magnet's direction can be found against other things, and so it is twisted in spin waves, split into domains and lost at a sharp Curie point. The Higgs field's direction defines the very labels by which it would be found, so nothing can tell one of its picks from another: it has no spin waves and no domains, and, with its mass far above the endpoint of the jump, it settled in a crossover.

In Use

An electric motor turns because two magnets that meet have an energy that depends on how they point (Volume One, Chapter 8, Section II). A coil carrying a current is a magnet, and set in the field of a permanent magnet it turns to line up. Switch the current's direction each half turn, and it turns on without stopping. Run the same machine the other way, turning the coil in the magnet's field by hand, by steam or by wind, and the changing field through the coil sets a current flowing in it: that is a generator. The strongest permanent magnets, of neodymium, iron and boron (Section VII), drive the motors of hybrid and electric cars and the generators of many wind turbines (standard accounts of permanent magnets). Their large coercivity keeps them magnetized against the fields of the coils they work beside, and their high remanence lets a small magnet do the work of a large one. They must be kept well below their Curie point, since a motor that runs hot enough loses its magnets' memory.

A hard drive stores each *bit* of information, the smallest piece of information, one choice between two, as a magnet's held direction. Its disk is coated with a thin film of small grains of a cobalt alloy, each a single domain with its easy axis set across the film, and a bit is a small patch of grains magnetized up or down. A writing head passes over the patch with a field strong enough to turn its grains, and the grains then keep their direction for years. They are held by the barrier of Section IV, the anisotropy energy for each unit of volume times the volume of a grain, which must stand far above kT. That barrier sets how small the grains can be made: grains too small would have a barrier of only a few times kT and would lose their direction to heat. So the size of a grain, and with it the number of bits on a disk, is set by the competition of the anisotropy against heat. The reading head finds each patch's direction by its effect on a stack of thin magnetic films whose electrical resistance is low when the films' magnetizations are parallel and high when they are opposed. The change

of a stack's resistance with the alignment of the stack's films is the giant magnetoresistance found in 1988 by Albert Fert and Peter Grünberg (Baibich et al., 1988; Binasch, Grünberg, Saurenbach and Zinn, 1989). Fert and Grünberg shared the Nobel Prize in Physics for 2007.

A transformer changes the voltage of an alternating current, raising it for the long lines that carry power across a country and lowering it again for the outlet in a wall. Two coils are wound on one ring of iron, and the current in the first coil magnetizes the iron, which carries the changing field through the second coil and sets a current flowing there. The iron gathers the field because its domains turn to follow a small field from the coil, which is why the ring is made of a soft magnet, iron with a little silicon in it. The alternating current sweeps the ring's magnetization up and down fifty or sixty times each second, round its loop of hysteresis, and each sweep turns the area of the loop into heat in the iron. So the softer the iron and the narrower its loop, the less of the power is lost. The ring is built of thin sheets with insulation between them, so that the changing field cannot also set large currents going round inside the iron itself. Every motor, generator, hard drive and transformer is a use of one result of this chapter: a crystal whose spins line up holds a direction, and how firmly it holds it, by its anisotropy and its walls, is chosen by the maker.

Summary

Every electron is a small magnet of one Bohr magneton, and an atom carries a net magnetic moment only when it has a partly filled subshell. Copper's electrons are paired, in its filled 3d subshell and in its band, so copper carries no moments and answers a magnet only by the weak diamagnetism of every material, which pushes it slightly away. Where atoms keep their moments and nothing between them lines the moments up, the crystal is a paramagnet, and a field lines up only a share of its moments that falls as one over the temperature, Curie's law (Box 8.1). Between neighboring atoms the electric push between electrons, sorted by their

spins through exclusion, does the lining up. Electrons with aligned spins keep apart and push each other less, between neighboring atoms as within one atom, while a bond shared between neighbors takes two electrons of opposite spin. The overlap of the atoms' states and the strength of the push, values set by each crystal, decide which wins, and Heisenberg's exchange constant J describes the outcome. A ferromagnet aligns every atom one way, an antiferromagnet alternates them, a ferrimagnet alternates unequal moments, and a paramagnet leaves them unaligned. Iron aligns because its 3d electrons form a narrow, partly filled band that passes Stoner's rule.

The laws treat every direction alike, and so does the exchange, yet the aligned crystal's state of least energy points one way. The crystal picks one of the equal easy directions that spin-orbit coupling and its own arrangement set: six along the cube edges in iron, eight along the cube diagonals in nickel, two along the hexagonal axis in cobalt. It holds that direction: each spin is held by its neighbors, and the direction by the whole crystal. The direction is a record, found against a compass and found again. It is kept, since its turning would take angular momentum from outside or carry a whole region over the barrier of the anisotropy. Heat raises the entropy of the unaligned arrangements, and each spin's alignment rests on its neighbors', so the alignment falls away faster as the temperature rises. It is lost at the Curie point, 1043 kelvin for iron, in a continuous change, at a point because no arrangement lies between a picked direction and none. The mean field of Box 8.2 gives the point, the growth of the alignment below it, and the Curie-Weiss law above it. Near the point the measured powers, the critical exponents, depend only on the dimension and on what orders. Slow twists of the held direction run through the crystal as spin waves, whose quanta, magnons, are collective excitations and the Goldstone bosons of the magnet's hidden symmetry. A magnet's own field costs energy that grows as its volume, and the walls between domains cost energy that grows as their area, so a large crystal divides into

domains and a small grain keeps one (Box 8.3, Figure 8.1). The walls' catching on flaws gives a magnet its memory: its remanence, its coercivity and its loop of hysteresis.

The magnet and the Higgs field share one structure: laws alike in every direction, and a ground state that is not. They differ in what can be found. The magnet's direction can be found against other things, and so it carries spin waves, splits into domains and is lost at a sharp Curie point. The Higgs field's direction defines the labels by which it would be found, so nothing can tell one of its picks from another, and with its mass far above the endpoint of the jump it settled in a crossover with no point. Which crystals align, and how strongly, are measured values of each crystal: its exchange, its anisotropy and its Curie point. The structure that sorts them, the free energy, exclusion and the held direction, is the same for all.

A magnet is one way that many particles, cooled, come to share one thing: a direction. The spins of a magnet's electrons are each one half, and each electron is excluded from another's state. Wholes made of an even number of particles of spin one half are not excluded. What do they do when cold?

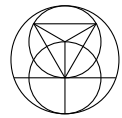
✶

KEY CONCEPTS

- **Magnetic moment.** How strong a small magnet a body is, measured by the turning push a magnetic field of a given strength gives it.
- **Bohr magneton.** $e\hbar/(2m_e)$, the moment of one unit $\hbar$ of orbital angular momentum, $9.2740100657 \times 10^{-24}$ joules for each tesla; the electron's spin carries one.
- **Tesla.** The unit of magnetic field; about one tesla at the face of a strong permanent magnet.
- **Magnetization; susceptibility.** The magnetic moment of each unit of volume; and the magnetization a field brings about for each unit of the field, as a pure number, negative for a material pushed away.

- **Paramagnet; Curie's law.** A substance whose atoms or molecules keep moments that nothing between them lines up, such as a salt whose metal ions have partly filled subshells, or liquid oxygen; its magnetization in a field grows as the field and falls as one over the temperature (Box 8.1).
- **Diamagnetism.** The weak answer of every material to a field, against the field, from the change the field makes in the motion of all its electrons.
- **Exchange; exchange constant.** The dependence of the electric push between electrons on their spins, through exclusion; J, the energy that the exchange gives to aligning two neighboring spins against opposing them, in the energy $-J\,S_1 \cdot S_2$ (Heisenberg).
- **Ferromagnet; antiferromagnet; ferrimagnet.** A crystal whose atoms' spins all line up one way; one whose neighboring spins alternate, with moments that cancel; and one whose alternating moments are unequal, so that they do not cancel.
- **Néel temperature.** The temperature below which an antiferromagnet's spins alternate.
- **Spontaneous symmetry breaking.** A symmetry of the laws that the state of least energy does not share: laws the same in every direction, and a ground state that is not; in a magnet the pick can be found, and in the Higgs field's settled value it cannot.
- **Magnetocrystalline anisotropy; easy axes.** The dependence of an aligned crystal's energy on the direction of its alignment relative to the crystal's axes, from spin-orbit coupling; the directions of lowest energy.
- **Mean field; Curie-Weiss law.** Each spin taken to feel its neighbors only through their average alignment, as a field in proportion to the magnetization; above the Curie point, a magnetization $C\,B/(T - T_C)$ (Box 8.2).
- **Curie point.** The temperature at which a magnet loses its alignment, at a point because a symmetry separates the arrangements.

- **Continuous change.** A change in which the order grows from nothing at a point fixed by a symmetry that separates the ordered arrangement from the disordered one, with no latent heat.
- **Critical exponents; universality.** The powers that describe a change of order close to its point; their depending only on the number of dimensions and on the kind of thing that orders, not on the material.
- **Spin wave; magnon.** A slow twist of a magnet's held direction running through the crystal; its quantum, a collective excitation that carries one unit ħ of spin, the Goldstone boson of the magnet's hidden symmetry.
- **Goldstone boson.** The quantum of a wave along a symmetry of the laws that the ground state hides, whose energy falls toward zero as the wave is made longer: among the particles a massless whole of spin zero, as the pions nearly are; in a magnet the magnon, a collective excitation that carries one unit ħ of spin.
- **Domain; domain wall.** A region of a magnet within which every spin points one way; the thin layer between two domains in which the spins turn from one direction to the other.
- **Remanence; coercivity; hysteresis.** The magnetization a magnet keeps with no field; the field the other way needed to bring it to zero; the lag of the magnetization behind the field, which makes it depend on the field's history.
- **Soft and hard magnets.** Magnets with a small coercivity and a narrow loop of hysteresis, which follow a field and give it up; and magnets with a large coercivity and a wide loop, which keep their magnetization.
- **Doublet.** A pair of kinds that the weak force turns into each other, such as the up and down quarks, or the electron and its neutrino; the Higgs field has one component for each side.
- **Gauge symmetry.** A symmetry whose rotations can be made separately at every place, so that the labels it defines turn with it; the Higgs field's direction in its doublet space is of this kind, and nothing can tell one of its picks from another.



Chapter 9

One Phase Across Many

CHAPTER OVERVIEW

Liquid helium cooled below 2.17 kelvin flows through the finest channels without friction. A ring of cold lead carries a current that has never been seen to fall. In this chapter we find why. A whole made of an even number of particles of spin one half is not excluded, so many such wholes, crowded and cold, gather into one lowest state. The gathering is a condensate: a large share of the wholes is in one state, and the whole gathering is described by one wave, with one amplitude and one phase across all of it (Box 9.1). The amplitude is the height of the wave at each place, and the chance of finding a whole there grows as its square. The phase is the stage of the wave's swing at a place, counted as a fraction of a whole turn. To slow such a condensate, some part of it must be lifted into a state above it. When the wholes push one another, the lowest such states are sound waves, whose energy grows in proportion to their momentum. A flow slower than the least ratio of energy to momentum among those states can lift nothing and lose nothing, so it flows without friction. In a gas of atoms that push one another gently, that least ratio is the speed of sound. Wholes that did not push one another would have no such safe speed. Because the phase is one across the condensate, the flow round any loop is counted in whole turns of the phase, in units of h/m. A spinning superfluid, a liquid that flows without friction because a large share of it is one state, fills with threads, each a whirl of one turn. Helium-4 is six particles of spin one half and gathers at 2.17 kelvin. Helium-3 is five

and cannot gather singly, so it waits until two atoms pair, which they do only below about a thousandth of a kelvin. In a metal the lattice's slow motion turns the electrons' push into a slight pull between electrons near the Fermi level. Two electrons near the top of the filled states bind under any pull however small, because every state below them is taken (Cooper's pair, Box 9.2). The pairs, each an even whole, share one phase. Breaking one costs at least twice the energy gap, the least energy that frees one electron from the shared state, which is about 1.76 times kT_c, with T_c the transition temperature below which the metal is a superconductor. A current in a superconductor is a twist of that one phase, and the twist is a form of the condensate, not a state above it. The current can lessen only by the phase slipping a whole turn, so the resistance to a steady current is zero at every temperature below the transition. Heavier isotopes make the lattice vibrate more slowly, narrowing the band of energy in which the pull acts while leaving its strength the same, so the transition falls as one over the square root of the nuclear mass. The shared state of pairs carries charge, and its phase is held by the whole metal. So a turn of the photon's kind, which turns the phase of every charged thing, changes the shared state and costs energy, and the photon gains a mass inside the metal. A magnetic field then reaches in only a thin layer, the penetration depth (Box 9.3): the Higgs field's way of giving a carrier its mass, seen again in a metal. The same turn of the photon's kind, made separately at each place with a matching change of the field's potential, fixes the form of Maxwell's four laws: the laws of the electric and magnetic field, which say how charges and their motion shape the field and how the field changes from place to place and in time (Box 9.4). In many superconductors the field enters as threads, each carrying one flux quantum, h/2e, a fixed amount of magnetic field passing through it, because each pair carries the charge 2e.

I. Flowing Without Friction

Chapter 8 ended with a question: wholes made of an even number of particles of spin one half are not excluded, so what do they do when cold? A particle's spin is the angular momentum it carries in itself, with no motion along a path (Chapter 1, Section IV), and electrons, protons and neutrons each have spin one half.

Pour liquid helium into a small cup and cool it below 2.17 kelvin. A film of the liquid, too thin to see, creeps up the inside wall of the cup, over the rim and down the outside, and drips from the bottom into the bath below, until the cup is empty (standard accounts of liquid helium). Push the same liquid through a plug of tightly packed powder, whose channels are far too fine for water to pass at any useful rate, and it flows through as if the plug were not there. In 1938 Pyotr Kapitza in Moscow, and John Allen and Don Misener in Cambridge, found that helium below this temperature flows through narrow slits with no friction that they could measure (Kapitza, 1938; Allen and Misener, 1938).

A second picture comes from metals. Cool a ring of lead below 7.2 kelvin, set a current going round it with a magnet, and take the magnet away. The current goes on flowing round the ring, with no battery to drive it, and it has never been found to fall: the measurements set a lower bound of more than 100,000 years on how long such a current lasts (File and Mills, 1963). Heike Kamerlingh Onnes found the first such metal in 1911, when the resistance of solid mercury vanished abruptly at 4.2 kelvin (Kamerlingh Onnes, 1911).

So the reader's question is this: how can a liquid flow without friction, and a metal carry current without loss?

The answer starts from three results already in hand. Volume One, Chapter 1, Box 1.2, found that a whole made of an even number of fermions, a fermion being a particle whose spin is an odd number of halves, is not excluded, so many such wholes can share one state (Chapter 1, Box

1.2, restates it). Chapter 2, Section XII and Box 2.5, found that bosons, a boson being a particle whose spin is a whole number, fill their states by the Bose-Einstein distribution. It found also that below a certain temperature a large share of them crowd into the one lowest state together, Bose-Einstein condensation. And Chapter 6 found that the electrons of a metal fill their band from the bottom up to a top, the filled states being called the Fermi sea and the energy of the top the Fermi level (Chapter 2, Section XII). So a perfect, motionless crystal offers no resistance, and real metals resist only through their vibrations and flaws. What is still needed is what one shared state does when it moves, why helium's two isotopes differ, and how electrons, which are fermions, come to share one state at all. And in Section XI we ask why a metal whose electrons share one state pushes a magnetic field out of itself, as the floating magnet of that section shows.

II. Even Wholes Gather into One State

Chapter 2, Section XII, pictured a campground that lets any number of campers pitch their tents on one spot, where on a cold night they crowd onto the best one. Bosons fill their states like the campers, and wholes made of an even number of fermions fill them the same way. How cold must a crowd of such wholes be before they crowd into one state, and what is the crowd like when they have?

A whole made of an even number of particles of spin one half is not excluded. Exchanging two such wholes, each in the same inner state, multiplies their joint state by (-1) raised to the number of fermions in each, which is $+1$ for an even number (Chapter 1, Box 1.2). The half units of spin pair into whole ones, so such a whole has a whole-number spin and is a boson (Chapter 1, Section V). An atom of helium-4 is such a whole, and so is an atom of rubidium-87, with its 37 protons, 50 neutrons and 37 electrons, 124 fermions in all. At energies too small to reach inside them, which is the case for atoms in a gas or liquid near the lowest temperatures, they behave as bosons.

When such wholes are crowded and cold, they gather into the lowest state. In Box 9.1 we find when.

Box 9.1. When even wholes gather into one state

Premises. (1) Bosons of one kind, of mass m, at temperature T and chemical potential μ, hold on average $1/(e^{(\varepsilon - \mu)/kT} - 1)$ in each state of energy ε, and μ lies below the lowest energy, here zero (Chapter 2, Box 2.5); the *chemical potential* is the energy that adding one more particle of that kind brings to the system when its entropy and its volume are held fixed (Chapter 2, Section XI). The system's *entropy* is the logarithm of the number of its microstates, its complete arrangements with every particle's state given, that share its totals, the *logarithm* of a number being the power to which a fixed base must be raised to give the number (Chapter 2, Section III). (2) In a box of volume V, a free particle has $V\, d^3p/h^3$ states of motion with momentum in each small range d^3p, with h the Planck constant (Chapter 2, Box 2.4). (3) The *thermal wavelength*, the length of the wave of a particle moving at the gas's typical speed (Chapter 2, Section XI), is written exactly as $\lambda = h/(2\pi mkT)^{1/2}$, read "lambda" (standard statistical mechanics). (4) The sum over every momentum of $1/(e^{p^2/(2mkT)} - 1)$, with the count of (2), is $V \times 2.612/\lambda^3$, where 2.612 is the value of a standard sum, the Riemann zeta function at three halves (mathematics).

Steps. By (1), every state above the lowest holds the most it can hold when μ reaches zero. By (2) and (4), the states above the lowest can then hold at most $2.612/\lambda^3$ particles in each unit of volume, and by (3) that number falls as the temperature falls, as $T^{3/2}$. If the wholes in each unit of volume, n, are more than that, the rest have nowhere to go but the lowest state. So the gathering into the lowest state begins where $n\lambda^3 = 2.612$: where the thermal wavelength has grown to about the spacing of the particles. Solving for the temperature: $T_c = (2\pi\hbar^2/(mk))\ (n/2.612)^{2/3}$. Below T_c, the share of the wholes in the lowest state is $1 - (T/T_c)^{3/2}$, since the states above hold only the amount that falls as $T^{3/2}$. For helium-4, with the liquid's density at the lowest temperatures, 0.145 grams for each cubic centi-

meter (Donnelly and Barenghi, 1998), and the atom's mass, 4.00260325413 atomic mass units (National Institute of Standards and Technology), n = 2.18×10^{28} atoms in each cubic meter, and $T_c = 3.13$ kelvin (computed).

Result. Wholes that are not excluded, crowded and cold, gather into the lowest state below the temperature $T_c = (2\pi\hbar^2/(mk))\ (n/2.612)^{2/3}$, at which their thermal wavelength reaches about their spacing: *Bose-Einstein condensation*. For atoms that did not push one another at helium-4's liquid density, the temperature would be 3.13 kelvin; helium-4 makes its change at 2.17 kelvin.

Fritz London made this comparison in 1938, proposing that what happens to helium-4 at 2.17 kelvin is this gathering into one state (London, 1938). The two temperatures are close but not equal, and the reason is that helium atoms in a liquid push one another hard, while Box 9.1 counts atoms that do not push at all. The pushing has a second effect that measurement shows. Near the lowest temperatures only about eight percent of the atoms of liquid helium-4 are in the lowest state of one atom's motion, against all of them for atoms that did not push (standard accounts of liquid helium, from neutron scattering). Two things are counted here, and they are kept apart in what follows. One is the share of the atoms in the lowest state of one atom's motion: about eight percent in liquid helium-4. The other is the state of the whole liquid, all its atoms taken together, which is one state with one wave across all of them. The push knocks most atoms out of the lowest state of motion, but it does not lift them into excitations, the states above the whole liquid's lowest that heat makes (Section III). The atoms it knocks out stay part of the whole liquid's one lowest state, which the push between the atoms shapes. So at the lowest temperatures there is nothing in the liquid but that one state, and Section III finds that the whole liquid then flows as one, not only its eight percent.

The plain case came in 1995. Eric Cornell and Carl Wieman cooled a thin gas of rubidium-87 atoms, held in a trap of magnetic fields, and on 5 June 1995 its condensate first appeared "near a temperature of 170 nanokelvin" (Anderson, Ensher, Matthews, Wieman and Cornell, 1995).

Wolfgang Ketterle made one of sodium atoms soon after (Davis et al., 1995), and the three shared the Nobel Prize in Physics for 2001. In a gas so thin the atoms push one another only gently, and nearly all of them gather into the lowest state as the gas is cooled far below its T_c.

What is the gathered crowd like? A large share of the wholes is in one state, and one state has one wave. The wave has one *amplitude*, the height of a particle's wave at each place, the chance of finding the particle there growing as its square (Volume One, Chapter 5, Section VII). It has one phase across the whole of it, the phase being the stage of a wave's swing at a place, counted as a fraction of a whole turn (Chapter 6, Section II). The many atoms together are one amplitude with one phase across the whole of the gathering. Such a gathering of many wholes into one state is a *condensate*. Its one phase can be seen. Two condensates of sodium released side by side expanded into each other's space and laid down stripes of high and low density, the pattern two waves make where they overlap, crests on crests and crests on troughs, as two sets of ripples on a pond do (Andrews et al., 1997).

So we now know what even wholes do when cold. Not excluded, they gather into the lowest state once their thermal wavelength reaches their spacing, and a large share of the gathering then becomes one state: one amplitude with one phase across the whole of it. For helium-4 the gathering comes at 2.17 kelvin, near the 3.13 kelvin of Box 9.1, and for thin gases of atoms at temperatures far lower.

III. Flow Without Loss

Hold a twig in a slow stream, and the water slides past it without a ripple. Hold it in a faster stream, and it trails a fan of small waves behind it, and the waves carry off some of the stream's motion. The twig can lose its motion to the water, or the water to the twig, only by making waves, and slow enough, it makes none. Why does a condensate flow past a wall without friction?

Friction is the passing of motion from a flowing liquid to the wall it flows past, or from a moving body to the liquid around it. For a condensate the passing has one way to happen. The condensate is one state, and to take motion from it, some part of the liquid must be lifted out of that state into a state above it: a sound wave, a whirl, a single atom knocked loose. Each such lifting makes an *excitation*, a definite amount of energy ε, read "epsilon", carried with a definite momentum p. Lev Landau saw what that requires (Landau, 1941). Take a body moving through the condensate at speed v. If it makes an excitation of momentum p, it gives up that momentum, and with it, for a body much heavier than the excitation, an energy of at most p times v. The excitation costs ε. So the body can make the excitation only if ε is no more than pv, that is, only if v is at least ε/p. If v is less than the least value of ε/p among all the excitations the condensate has, no excitation can be made at all, nothing can be lost, and the condensate flows past the body without friction. That least ratio of energy to momentum is the condensate's safe speed, its *Landau critical velocity*.

Which condensates have a safe speed above zero? Those whose wholes push one another, and the reason shows what flow without loss needs. In a crowd that pushes back, a slow, long disturbance is a sound wave, a motion shared by all the wholes together, and the energy of its quantum grows in proportion to its momentum: $\varepsilon = c_s p$, with c_s the speed of sound. For sound, ε/p is c_s at every momentum, so the safe speed is at most the speed of sound. In a gas of atoms that push one another only gently, where sound is the only low excitation, the safe speed is the speed of sound. The push gives the safe speed by making every low excitation carry much momentum for its energy. Sound waves of every small energy lie just above the condensate, so the safe speed comes from that ratio and from no gap in energy. For wholes that did not push one another, the lowest excitations would be single wholes lifted into slow motion, with energy $p^2/(2m)$, so ε/p would be $p/(2m)$, which falls to zero for the slowest

motions. A body moving at any speed, however slow, could make some of them, and such a condensate would have no safe speed. So the push between the wholes is what makes flow without loss possible.

Helium-4 shows both kinds of excitation. Its long excitations are sound, which in the liquid travels at about 238 meters each second (Donnelly and Barenghi, 1998), and whose quanta are called phonons, as in a crystal. Each is a collective excitation, a motion shared by many particles at once that comes in quanta (Chapter 5, Section IV). At shorter wavelengths, about the spacing of the atoms, the energy of an excitation rises less steeply and then falls to a least value before it rises again. Landau named the excitations near that least value *rotons*, and their least energy is k times about 8.6 kelvin, at a momentum ħ times about 1.9 for each ångström, a tenth of a nanometer (Donnelly and Barenghi, 1998). For rotons the ratio ε/p is about 59 meters each second (computed), below the speed of sound. So in helium-4 the rotons set the least ratio, and the safe speed for a small body moving through the liquid is near that value. Real flows through tubes and slits break down at far lower speeds, of order 20 centimeters each second (standard accounts of liquid helium). They lose their motion first by making whirls in the liquid, the threads of Section IV, which are excitations too and are easiest to make where the flow meets a wall.

At any temperature above the lowest, heat itself makes some of these excitations. A crowd of phonons and rotons moves about in the liquid, and that crowd does feel friction and does carry the liquid's entropy. So below 2.17 kelvin helium-4 behaves as two liquids at once that pass through each other (Tisza, 1938; Landau, 1941). The *normal part* is the crowd of excitations, which has viscosity and carries all the entropy. The *superfluid part* is the condensate's flow, which has neither, a *superfluid* being a liquid that flows without friction because a large share of it is one state. The picture of helium-4 as a normal part and a superfluid part is the *two-fluid model*. The superfluid part is the whole liquid at the lowest temperatures, where heat makes no excitations at all, and none of it at 2.17 kelvin. Two liquids that pass through each other can also move against

each other. If the superfluid part flows one way while the normal part flows the other, the liquid's density stays the same, but its entropy, carried by the normal part alone, moves, and so does its temperature. That wave of temperature, with no wave of pressure, is *second sound*, which travels at about 20 meters each second near 1.8 kelvin, as Vasily Peshkov measured it in 1944 (Peshkov, 1944). Second sound is the plainest sign that the two parts are real: an ordinary liquid carries a change of temperature only by the slow diffusion of heat (Chapter 7, Section III), and helium-4 below 2.17 kelvin carries it as a wave.

So we now know why a condensate flows without friction. To slow it, some part must be lifted into an excitation, and a flow slower than the least ratio of energy to momentum among the excitations cannot make one. When the wholes push one another, the lowest excitations are sound waves with energy in proportion to momentum, so that least ratio stands above zero, at the speed of sound or, in helium-4, at the rotons' lower ratio. Wholes that did not push one another would have no safe speed, so the push between them is needed for flow without loss.

IV. Whole Turns of the Flow

Volume One, Chapter 1, Section V, watched the minute hand of a clock: in one hour it makes one whole turn and stands exactly where it began, so the angle it sweeps in any number of hours is a whole number of turns. An angle that must come back to itself counts in whole turns. A condensate has one phase across the whole of it, and a phase is an angle. What does that do to the way the condensate can flow round a loop?

The flow of a condensate is written in its phase. A wave's momentum is $\hbar$ times the rate at which its phase advances along it, the phase counted in radians, 2π to a whole turn (standard quantum mechanics). So a condensate of wholes of mass m flows at the speed $v = (\hbar/m)$ times the rate

at which its one phase changes from place to place. Where the phase is the same everywhere, the condensate is at rest; where it advances steadily along a direction, the condensate flows that way.

Now follow the phase round a closed loop inside the condensate. At each place the condensate has one phase, so on coming back to the starting place the phase must come back to the value it had there. The total change of phase round the loop is therefore a whole number of turns, $n \times 2\pi$, with n a whole number, zero included. Adding up the flow along the loop, speed times length, gives $(\hbar/m)$ times that total change of phase, so the flow round any loop is $n \times 2\pi\hbar/m = n\ h/m$. The flow round a loop in a condensate is counted in whole units of h/m, the Planck constant over the mass of one whole (Onsager, 1949; Feynman, 1955). For helium-4 the unit is 9.97×10^{-8} square meters each second (computed from the Planck constant and the atom's mass). Henry Hall and William Vinen found the threads of flow that the next paragraph finds, in 1956, by the way they hold back second sound in a spinning vessel of superfluid helium (Hall and Vinen, 1956). In 1961 Vinen measured the flow round a single thread and found it one unit h/m (Vinen, 1961).

A loop round which the phase winds n turns cannot be shrunk to a point inside the condensate without the phase having somewhere to unwind. So at the center of such a loop there must be a line where the condensate is missing: a thread whose amplitude falls to zero along its axis, round which the liquid whirls. Such a thread is a *quantized vortex*, and in helium its core, where the amplitude is lost, is a few ångströms across (standard accounts of liquid helium). Each atom whirling round a thread of one turn at a distance r moves at speed $h/(2\pi mr)$. So its angular momentum about the thread is $m \times h/(2\pi mr) \times r = \hbar$: one whole unit of angular momentum, the whole unit that Chapter 1, Section V, found for every motion along a path.

Spin a bucket of superfluid helium. An ordinary liquid in a spinning bucket comes to turn with the bucket as a solid body does, and its flow round a loop then grows in proportion to the loop's area, by any amount

at all. The superfluid's flow round every loop must be a whole number of units, so it does the nearest thing it can: it fills with threads, each a vortex of one turn, set parallel to the axis of spin and spaced so that, on average, the liquid turns as the bucket does. The number of threads in each unit of area is twice the bucket's rate of turning, in radians each second, divided by h/m (Feynman, 1955): for a bucket turning once each second, about 126 threads in each square millimeter (computed). Richard Packard and his colleagues photographed the ends of such threads where they met the liquid's surface, set out in a regular array (Yarmchuk, Gordon and Packard, 1979).

So we now know how a condensate can flow round a loop. Its one phase must come back to itself round any loop, so the flow round every loop is a whole number of units h/m. Where the flow winds, it winds round threads of missing condensate, each a vortex of whole turns, and each atom of a one-turn vortex carries one unit ħ of angular momentum about it.

V. The Two Heliums

Two flasks hold helium, the same element, with the same chemistry: neither will join any other atom, and both stay liquid at ordinary pressure down to the lowest temperatures there are. The atoms in the two flasks differ by one neutron each. Cooled below 2.17 kelvin, the helium in the first flask creeps out of its cup. The helium in the second, cooled to the same temperature, flows as any liquid does, with friction, and goes on doing so a thousand times colder. Why does one neutron make that difference?

Isotopes are different forms of one element, with the same number of protons and different numbers of neutrons (Chapter 1, Section VIII); Chapter 12 follows them further. *Helium-4* is the isotope whose atom has two protons and two neutrons in its nucleus and two electrons round it: six particles of spin one half, an even number. So the helium-4 atom is not

excluded, by the rule of Volume One, Chapter 1, Box 1.2, and it is a boson. Cooled enough, its atoms gather into one shared state, as Section II found, and the liquid flows without friction, as Section III found: it becomes a superfluid. Helium-4 makes that change at 2.1768 kelvin at the pressure of its own vapor (standard tables of liquid helium); the 2.17 kelvin of Section I is that value written to its first two decimal places.

Helium-3 is the isotope whose atom has two protons and one neutron in its nucleus and two electrons round it: five particles of spin one half, an odd number. So the helium-3 atom is excluded, as a fermion is, and its atoms cannot gather into one state singly. Cooled, liquid helium-3 fills its states as the electrons of a metal fill theirs, one atom to each state, up to a Fermi level, and it flows with friction as an ordinary liquid does. It is the liquid that Chapter 2, Section XIV, met, in which nearly every filled state of motion holds two atoms of opposite nuclear spin, so that the spins have almost no free choices left. Squeezing that liquid into a solid, where each spin is free again, takes in heat and cools it.

Helium-3 can gather into one state only when two of its atoms bind into a pair, since a pair of two helium-3 atoms holds ten particles of spin one half, an even number, and is not excluded. The pairing of helium-3 atoms is so weak that it holds only below about a thousandth of a kelvin, against 2.17 kelvin for helium-4's gathering into one state. At zero pressure liquid helium-3 becomes a superfluid near 0.93 thousandths of a kelvin (Greywall, 1986). Squeezed to the pressure at which it begins to freeze, the pressure of its melting curve, it becomes a superfluid at 2.491 thousandths of a kelvin (standard tables of the helium-3 superfluid). The two figures show that the change moves with the pressure, and that at every pressure it lies within a few thousandths of a kelvin, a thousand times colder than helium-4's. Douglas Osheroff, Robert Richardson and David Lee found it in 1972, in a cell cooled by squeezing the liquid into a solid, the cooling of Chapter 2, Section XIV (Osheroff, Richardson and Lee, 1972). They saw two changes along the melting curve, which their thermometers placed near 2.7 and 1.8 thousandths of a kelvin. The first

change is the change into the superfluid, and the second change is a change from one superfluid form of the liquid into another. Osheroff, Richardson and Lee shared the Nobel Prize in Physics for 1996.

The pairs of helium-3 differ from the pairs of electrons that Section VIII finds in ordinary metals. Each helium-3 atom carries the spin one half of its nucleus, and in the pair the two spins point the same way, with total spin one. The two atoms go round each other with one unit ħ of orbital angular momentum (standard accounts of the helium-3 superfluid). What makes the pair an even whole is only that it holds an even number of particles of spin one half. The directions of their spins can be opposite, as in ordinary metals, or aligned, as here.

So we now know why the two heliums differ at their coldest. Helium-4 is six particles of spin one half, an even number, so its atoms are not excluded and gather into one state at 2.17 kelvin. Helium-3 is five, an odd number, so its atoms are excluded and gather into one state only once two of them pair, which happens only below about a thousandth of a kelvin. What separates the two at their coldest is the count of particles of spin one half in each atom, odd or even.

VI. A Pull Through the Lattice

Roll a heavy ball across a soft mattress. It presses a trough into the mattress as it goes, and the mattress, slow to spring back, keeps the trough for a moment after the ball has passed. Roll a second ball along the same way a moment later, and it drops into the trough the first ball left: the second ball is drawn after the first, though the two never touched. How can two electrons, which push each other away, come to pull each other together in a metal?

The question is forced by what metals do. Below a definite temperature some metals carry a steady current with no resistance at all, and, as Section XI finds, push a magnetic field out of themselves: they are *superconductors*. The temperature below which a metal is a superconductor is

its *transition temperature*, written T_c. Measured transition temperatures of the elements are low: 1.20 kelvin for aluminum, 3.72 for tin, 4.15 for mercury, 7.19 for lead and 9.26 for niobium (standard tables of superconductors). The carriers of a metal's current are its electrons, and electrons are fermions, excluded from sharing a state, so they cannot gather into one state singly, as helium-3's atoms cannot. Section V found the way helium-3 takes: two of its atoms pair into an even whole. For electrons to do the same, two electrons must attract each other, though their charges push them apart.

The metal's lattice supplies the pull. The lattice is a crystal of positive ions, each an atom that has given its outer electrons to the band, and the ions can move a little about their places, as the vibrations of Chapter 5 move them. An electron moving through the lattice draws the positive ions near its path slightly toward it. The ions are thousands of times heavier than the electron and slow to answer, so they are still drawn together, and still slow to spring back, after the electron has gone on. The electron leaves a trail of slightly crowded positive charge behind it, as the ball leaves its trough. A second electron passing near that trail is pulled into it (Fröhlich, 1950). The two electrons also push each other directly, but in a metal that push is cut short by screening, charges which gather round a charge and cancel its field at a distance (Chapter 1, Section VII), here the other electrons of the band. And the pull through the lattice acts later and farther along the path, after the first electron has moved away. So between two electrons near the Fermi level, the slow pull through the lattice can outweigh their screened push, and the net is a slight attraction.

The pull acts only between electrons whose energies differ by no more than the lattice's vibrations can carry. The highest frequency of the lattice's vibrations is f_D, with $hf_D = k\Theta$, where Θ is the Debye temperature, the temperature at which $k\Theta$ equals the quantum of a crystal's highest mode (Chapter 5, Section V). For lead Θ is 105 kelvin (Kittel, 1996), so the pull acts only within about 0.009 electron volts of the Fermi level (computed).

A band within about 0.009 electron volts of the Fermi level is narrow against lead's Fermi level, some electron volts above the bottom of lead's band.

The same coupling of electrons to the lattice's vibrations that makes the pull also makes resistance, since Chapter 6, Section VIII, found that a metal's resistance at ordinary temperatures comes from its electrons being turned aside by those vibrations. So the metals that resist most at room temperature, such as lead and niobium, are among the best superconductors. The metals that conduct best, copper, silver and gold, have not been found to superconduct at all at ordinary pressure (Kittel, 1996): their electrons are coupled too weakly to the lattice to pair.

So we now know where the attraction between electrons comes from. An electron moving through the lattice draws the slow, heavy ions toward its path and leaves a trail of positive charge, which draws a second electron after it. With the electrons' direct push screened, two electrons near the Fermi level, within the band of energies the lattice's vibrations reach, attract each other slightly.

VII. Cooper's Pair

Volume One, Chapter 4, Section VIII, pictured a ball rolling in a shallow hollow: a pull of short reach holds a particle only if the hollow is deep enough, because confining the particle costs energy, and a shallow hollow lets it roll out. The rule of the shallow hollow, for two particles, is *Bargmann's bound*: a pull of short reach binds two particles only when the pull's strength passes a threshold, because confinement costs energy. The pull between two electrons in a metal is far too slight to pass any such threshold in empty space. How, then, can it bind them?

In 1956 Leon Cooper saw what the metal adds (Cooper, 1956). Every state below the Fermi level is already taken, so two electrons just above it cannot fall into any of those states: they have nothing lower to fall to, and the attraction alone decides. In Box 9.2 we follow the two electrons.

Box 9.2. Cooper's pair

Premises. (1) Two electrons, of opposite spin and opposite momentum, so that the pair is at rest as a whole, are added to a metal whose every state below the Fermi level is filled; by exclusion they can take only states above it (Volume One, Chapter 1, Box 1.2; Chapter 6, Section IV). (2) The pull of Section VI acts with one strength, V, between any two states of the pair whose energies lie above the Fermi level by less than the energy of the lattice's highest vibration, $\hbar\omega_D = k\Theta$, read "h-bar omega D", and not otherwise (Cooper, 1956). (3) Near the Fermi level, the electron states of one direction of spin number N(0) in each small range of energy, nearly the same across the narrow band of (2) (Chapter 6, Section IV, the density of states); the product N(0)V, read "N nought V", is a pure number that measures the pull's strength against the room it has to act in. (4) For positive E_b and a, the sum over energies ξ, read "xi", from 0 to a, of $1/(2\xi + E_b)$ for each small range of ξ, is $(1/2)\ \ln((2a + E_b)/E_b)$, with ln the natural logarithm (mathematics).

Steps. Write the pair's state as a sum over its allowed states, each with a weight, and let ξ be the energy of each electron above the Fermi level. Seek a bound pair whose energy lies an amount E_b, read "E b", the binding, below that of two electrons at the Fermi level. Each weight then satisfies $(2\xi + E_b) \times$ weight = V × (the sum of all the weights), since the pull of (2) links every allowed state to every other with the same strength. Dividing by $2\xi + E_b$ and adding over every allowed state gives 1 = V × (the sum over allowed states of $1/(2\xi + E_b)$). By (3) and (4), that sum is N(0) times $(1/2)\ \ln((2\hbar\omega_D + E_b)/E_b)$, so $1 = (N(0)V/2)\ \ln((2\hbar\omega_D + E_b)/E_b)$. The logarithm grows without bound as E_b shrinks toward zero, so for every positive V, however small, there is a binding E_b above zero that meets the equation: $E_b = 2\hbar\omega_D/(e^{2/(N(0)V)} - 1)$, which for a slight pull is close to $2\hbar\omega_D e^{-2/(N(0)V)}$. For two particles in empty space the count of states falls to zero at the lowest energy, so the same sum stays finite as E_b shrinks, and a pull too slight leaves no solution: that is Bargmann's bound.

The filled states take away everything below the Fermi level and leave the pair a count of states that does not fall to zero at its lowest energy, so the sum grows without bound and any pull binds.

Result. Two electrons just above a filled Fermi sea form a bound pair under any attraction however small, with a binding of about $2\hbar\omega_D e^{-2/(N(0)V)}$: they have nothing lower to fall to, and the attraction alone decides. The binding is far smaller than the vibrations' energy $\hbar\omega_D$ when the pull is slight, since it falls as an exponential of one over $N(0)V$.

A pair of two electrons bound in this way is a *Cooper pair*. It holds two particles of spin one half, an even number, so it is an even whole, not excluded, as the helium-3 pair of Section V is. In the ordinary metals of this chapter the two spins of a pair are opposite, as Box 9.2 takes them, and the pair carries no orbital angular momentum. The evenness alone does not require opposite spins, and the helium-3 pair's aligned spins show the other case.

So we now know how two electrons that push each other apart come to be bound. With every state below the Fermi level taken, two electrons just above it have nothing lower to fall to, and the slight pull through the lattice, however small, binds them into a Cooper pair, an even whole.

VIII. The Pairs Share One Phase

In a crowded ballroom every couple dances the same figure in time to the same music, so that the whole floor turns as one. The two partners of each couple hold hands across the room, with thousands of other dancers between them, and every dancer belongs to some couple. No couple could be lifted out of the dance without stopping two dancers and breaking a hold that every other couple keeps. What do all the pairs of a metal do together?

Box 9.2 bound two electrons above a quiet sea. In a metal every electron near the Fermi level feels the same pull, so all of them pair at once. Since each pair is an even whole, not excluded, the pairs gather into one state, as the helium-4 atoms of Section II do: the metal's paired electrons become one amplitude with one phase across the whole piece of metal. John Bardeen, Leon Cooper and Robert Schrieffer found that state in 1957 (Bardeen, Cooper and Schrieffer, 1957), and their account of superconductivity is called the *BCS theory*, from their initials.

A pair is large. The distance over which the two electrons of a pair are held together, the pair's size, is the *coherence length*: about 1,600 nanometers in aluminum, 83 in lead and 38 in niobium (Kittel, 1996). Within the extent of one pair in aluminum lie about 10^{12} other electrons (computed from aluminum's 1.8×10^{29} outer electrons in each cubic meter), so the pairs overlap enormously, as the dancers' couples do, and together they make one condensate of the whole metal. The pairing and the sharing of one phase happen together, and each holds the other. The pairs form within the shared state, as the couples of the ballroom dance only within the one figure, and not as small molecules that first form and then gather.

Breaking one pair costs energy. Lifting one electron of a pair out of the shared state means taking it out of a state in which every pair holds every other. The least energy this takes, for each electron so freed, is the *energy gap*, written Δ, read "delta", so breaking a pair, which frees two electrons, costs at least 2Δ. The BCS theory predicts the gap at the lowest temperature to be $\Delta = 1.764\ kT_c$, in proportion to the transition temperature (Bardeen, Cooper and Schrieffer, 1957), so that $2\Delta = 3.53\ kT_c$. For aluminum this gives $\Delta = 0.18$ thousandths of an electron volt (computed from its 1.20 kelvin), and for lead 1.09 thousandths (computed from its 7.19 kelvin). The BCS ratio is the ratio for a slight pull, the pull of Box 9.2, and the more strongly a metal's electrons are coupled to its lattice, the larger the measured ratio. Measured, 2Δ is 3.4 times kT_c for aluminum, whose electrons are coupled to the lattice only slightly, and 4.3 times for lead, whose electrons are coupled strongly (Kittel, 1996). Ivar Giaever meas-

ured the gap directly by passing electrons through a thin insulating layer from a normal metal into a superconductor: almost no current flowed until the voltage gave each electron enough energy to reach the states above the gap (Giaever, 1960). The gap also shows in light: a superconductor takes up light only above the frequency $2\Delta/h$, 88 gigahertz for aluminum (computed), and below it nothing in the metal can take up the light's energy. The gap shrinks as the temperature rises, as heat breaks more pairs and leaves fewer to hold the rest, and it closes at T_c.

So we now know what all the pairs do together. Every electron near the Fermi level pairs, the pairs are even wholes, and they gather into one state with one amplitude and one phase across the metal. The pairs are large and overlap enormously. Breaking a pair costs at least twice the gap, about 3.5 times kT_c.

IX. Why the Current Does Not Die

Lay a garden hose in a ring on the lawn, with a painted stripe running along it, and give the stripe a whole number of twists round the ring before joining the ends. Shake the hose, bend it, pull it about: the stripe's twists slide along, bunch up and thin out, but their number round the ring stays the same. Only cutting the hose and rejoining it can change the number. Why does a current in a superconducting ring go on for years?

The answer needs two results. The first result is the gap. Below the transition, the pairs survive because breaking one costs at least 2Δ, and the lattice's vibrations and flaws, which take a normal electron's motion and give resistance (Chapter 6, Section VIII), can take motion from the shared state only by breaking pairs. The gap is the reason the pairs last. The current needs a second result, since a little above absolute zero heat does break some pairs, and close to T_c it breaks many.

Section IV found that a condensate's flow is written in its phase: it flows where its one phase advances from place to place. A current in a superconductor is a slow twist of the pairs' one phase along the wire. Such a

twist is the shared state itself, with its phase advancing along the metal: a form of the one state, and not a state above it, since nothing is lifted out of it. So carrying a current breaks no pair and makes no excitation. In a ring, the phase must come back to itself round the ring, so its twist round the ring is a whole number of turns, as the stripe's is, and that whole number sets the current. To make the current smaller, the number of turns must fall by one: somewhere in the ring the phase must slip a whole turn. For the phase to slip, the shared state must vanish, for an instant, across a whole cross-section of the wire. That breaks the pairs in a slab of metal across the wire, and the energy it takes grows with the number of pairs in the slab. The weight with which heat makes such a change is the Boltzmann factor of an energy in proportion to that number (Chapter 2, Section X). For any wire of ordinary size that weight is far too small for the change to happen in any time that could be waited. Because the weight of a slip of the phase is so small, the current in the lead ring of Section I has never been found to fall.

This holds even though heat breaks some pairs. Their electrons move as the electrons of a normal metal do, and they carry a share of any current with resistance. But they carry it side by side with the shared state, which carries current with none. A steady current through two paths side by side, one of which has no resistance at all, goes wholly by that one, with no voltage across either. So for a steady current the resistance is zero at every temperature below the transition, however close to it, though heat breaks some pairs. A current that changes direction rapidly does lose a little to the broken pairs, since the shared state needs a voltage to change its twist.

Above the transition temperature the pairs break, the shared state is gone, and the metal resists as before. Onnes saw that in mercury: its resistance, falling smoothly as the metal was cooled, vanished abruptly at 4.2 kelvin, and returned when the metal was warmed again above that temperature (Kamerlingh Onnes, 1911). A metal that carries a steady current with zero resistance below its transition temperature shows *superconductivity*.

So we now know why a superconductor carries current without loss. The pairs survive because breaking one costs at least twice the gap. The current lasts because it is a twist of the one phase of the shared state, a form of the state and not a state above it, which can lessen only by the phase slipping a whole turn across the wire. The pairs that heat breaks carry current only beside the shared state, which shorts them out, so the resistance to a steady current is zero at every temperature below T_c.

X. Heavier Nuclei, a Lower Transition

Chapter 3, Section VI, hung a light weight and a heavy weight on two springs of the same stiffness: the heavier weight bounces more slowly. The nuclei of a metal's atoms are the weights of its lattice, and an isotope with more neutrons is a heavier weight on the same springs, since the springs are made by the electrons, which are the same for every isotope. If the pull between electrons comes through the lattice's vibrations, the mass of the nuclei should show in the transition temperature. Which way, and by how much?

The BCS theory gives the transition temperature in terms of the two quantities of Box 9.2: $kT_c = 1.13\ \hbar\omega_D\ e^{-1/(N(0)V)}$ (Bardeen, Cooper and Schrieffer, 1957). The transition temperature is in proportion to the width of the band of energy in which the pull acts, $\hbar\omega_D$, the energy of the lattice's highest vibration, and it depends on the pull's strength through the exponential. So the question is what a heavier nucleus does to each.

The width of the band falls. A weight of mass M on a spring of stiffness K swings at the angular frequency $(K/M)^{1/2}$, so every vibration of the lattice, the highest included, is slower for heavier nuclei, as one over the square root of M.

The strength of the pull stays the same. The pull is made by the ions' answer to an electron's charge: a force F on an ion held by a spring of stiffness K moves it by F/K. The stiffness is set by the electrons that bind the ions in place, the same for every isotope, and it equals $M\omega^2$. So the ion's

answer, $F/(M\omega^2)$, is the same for every isotope though M and ω each change: a heavier nucleus answers more slowly, but just as far. So $N(0)V$ is the same for every isotope of a metal.

Together: heavier nuclei give slower vibrations, so the band of energies in which the pull acts is narrower, while the pull within it is just as strong. The transition temperature falls in proportion to the band's width, T_c in proportion to $M^{-1/2}$: the same metal made with heavier isotopes becomes a superconductor at a lower temperature. The lower transition temperature of a metal made with heavier isotopes is the *isotope effect*. It was found in 1950, before the BCS theory, in mercury made of different isotopes (Maxwell, 1950; Reynolds, Serin, Wright and Nesbitt, 1950), and it showed that the lattice takes part in superconductivity. The measured rule in such metals is the one found here, the transition temperature in proportion to one over the square root of the nuclear mass. The size of the isotope effect measures how much of the pull comes through vibrations like those of simple springs. Where the electrons' screened push, or vibrations unlike those of simple springs, weigh more, the effect is smaller: ruthenium and zirconium show almost none (Kittel, 1996). In palladium filled with hydrogen the effect is reversed, a higher transition with the heavier deuterium (Stritzker and Buckel, 1972). For mercury, from atoms of mass 198 to atoms of mass 204, the one-half power gives a transition lower by 1.5 percent, about 0.06 kelvin (computed).

So we now know which way the mass of the nuclei moves the transition. Heavier nuclei vibrate more slowly, which narrows the band of energy in which the pull through the lattice acts, while the pull's strength, set by the ions' answer $F/(M\omega^2)$, stays the same. So the transition temperature falls as one over the square root of the nuclear mass. The superconductivity of an ordinary metal depends on the mass of its nuclei, a property of the nucleus seen in matter, and Chapter 12 follows the other ways the nucleus shows through the electrons that hide it.

XI. The Field Kept Out: The Higgs Settling in a Metal

Set a black ceramic disk in a shallow dish, pour liquid nitrogen over it, and lay a small magnet above it. The magnet floats, a few millimeters over the disk, held up by nothing that can be seen. The disk has become a superconductor, and it pushes the magnet's field out of itself. The field, crowded between the disk and the magnet, holds the magnet up. Why does a superconductor keep a magnetic field out?

Walther Meissner and Robert Ochsenfeld found in 1933 that a metal cooled through its transition while sitting in a field pushes the field out of itself as it becomes a superconductor (Meissner and Ochsenfeld, 1933). The pushing out of the field is the *Meissner effect*. The Meissner effect makes a superconductor a perfect diamagnet, whose susceptibility, in the sense of Chapter 8, Section II, is -1, since the field inside the superconductor is zero, except in a thin layer at the superconductor's surface.

The reason lies in the one phase of the shared state. A magnetic field acts on a charged wave through the field's *potential*, an arrow at each place from which the magnetic field follows (Volume One, Chapter 8, Box 8.1). The magnetic field through a small loop is how much the potential turns round that loop: the potential's *curl*, the curl at a place being how much a quantity turns round a small loop there, for each unit of the loop's area. For a charged wave, the phase and the potential are never measured apart. A charged wave's speed is $\hbar$ times the rate at which its phase changes from place to place, less its charge times the potential, all divided by its mass (Box 9.3, premise 2). So a turn of the phase that differs from place to place, made together with a matching change of the potential, leaves every speed as it was and changes nothing that any measurement can find (Weyl, 1929; standard electromagnetism of charged waves). The matched turn of the phase and change of the potential is the tower clock of Chapter 8, Section VIII, now for the phase of a charged wave. The matched pair of changes is a rotation of gauge symmetry. In the shared state of pairs, the

phase is one across the metal, held by the whole. A magnetic field inside the metal would make the potential wind round every loop that enclosed some of the field. For the pairs to stay at rest, the phase would have to wind round each such loop to match, and the phase cannot wind round a loop without a thread at its center where the shared state is missing (Section IV). So the pairs move, and their motion is a current. The shared state answers a field with currents at its surface, whose own field cancels the field inside, except in a thin layer. Box 9.3 finds the layer.

Box 9.3. The field kept out

Premises. (1) The pairs of a superconductor share one state with one phase across the metal; the n electrons in each unit of volume that share it make $n/2$ pairs, each of charge of size $2e$ and mass $2m_e$ (Sections VII and VIII). (2) A charged particle in a magnetic field moves with the speed (its momentum less its charge times the potential A) divided by its mass, the potential's part entering with the charge (Volume One, Chapter 8, Box 8.1); for a wave the momentum is $\hbar$ times the rate at which the phase changes from place to place (Section IV); and where the phase is one across the metal and does not wind, the rate of change of the phase can be taken as zero, by changing phase and potential together (standard electromagnetism of charged waves). (3) The curl of the magnetic field is μ_0 times the current in each unit of area, Ampère's law, with μ_0 the magnetic constant (standard electromagnetism). (4) The plasma frequency of n electrons in each unit of volume is $\omega_p = (ne^2/(\varepsilon_0 m_e))^{1/2}$ (Chapter 4, Section IX), and $\mu_0\varepsilon_0 = 1/c^2$, with c the speed of light (standard electromagnetism).

Steps. By (1) and (2), the pairs move with the speed $-(\text{charge} \times A)/(2m_e)$, and the current in each unit of area is $(n/2) \times \text{charge} \times \text{speed} = -(n/2)(2e)^2A/(2m_e) = -(ne^2/m_e)A$: the current is in proportion to the potential, against it (London and London, 1935). Taking the curl of both sides, the curl of the current is $-(ne^2/m_e)B$. By (3), the curl of the curl of B is μ_0 times the curl of the current, $-\mu_0(ne^2/m_e)B$; for a magnetic field, which has no sources, the curl of the curl is minus the field's second rate of

change from place to place, so that rate of change is B/λ^2, with $\lambda = (m_e/(\mu_0 n e^2))^{1/2}$. Just inside a flat face of the metal, with the field along the face, the field that meets this and does not grow without bound inside is $B(x) = B_0 e^{-x/\lambda}$, with x the depth below the face. By (4), $\lambda = c/\omega_p$. For aluminum, counting its three outer electrons for each atom, 1.81×10^{29} in each cubic meter, $\lambda = 12.5$ nanometers (computed).

Result. A magnetic field reaches into a superconductor only a thin layer, falling by the factor e = 2.718 for each depth λ, the *penetration depth*. Counted with every outer electron sharing the phase, λ is the speed of light divided by the plasma frequency, about ten nanometers for an ordinary metal. Measured penetration depths are typically 50 to 500 nanometers (standard tables of superconductors), longer because in a real metal the shared electrons answer with the band's effective mass and over the size of a pair, not at a point. A field that falls as $e^{-x/\lambda}$ is the field of a carrier whose *own length*, $\hbar/(mc)$, the length that the carrier's mass, $\hbar$ and c make together (Volume One, Chapter 1, Section III), is λ: inside the superconductor the photon acts as a carrier of mass $m_\gamma = \hbar/(\lambda c)$, read "m gamma", whose rest energy $m_\gamma c^2 = \hbar c/\lambda$ is 3.9 electron volts for $\lambda = 50$ nanometers and 0.39 for $\lambda = 500$ nanometers (computed).

A carrier that gains a mass from a settled value filling space is what *The Coming of the Kinds* has already found for the Higgs field, and it has stated the rule. In its Chapter 6, Section III, the Higgs field gives the carriers of the weak force their masses by this rule: "A carrier becomes massive when the settled value of the field tells apart the states it rotates among". In that rule a carrier rotates among states: a carrier acts by turning one state of a particle into another, and each such turning is a rotation (*The Coming of the Kinds*, Chapter 6, Section III). The settled value tells apart the states a carrier rotates among when every such rotation changes the settled value and so costs energy. The photon stays massless in empty space because the Higgs field's value carries no electric charge: in the zoo's words, quoted there, "The combination that reads electric charge

finds nothing in the condensate to read, and stays massless. That combination is the photon" (Level 8, Section III). The photon's rotation is the turning of the phase of every charged thing by an amount in proportion to its charge, made separately at every place, which is the rotation of gauge symmetry above. Inside a superconductor there is something charged to read: the shared state of pairs, each pair of charge 2e, with one phase held across the metal. Turning the phase of the pairs by different amounts at different places, with the potential left as it was, sets the pairs moving, and their motion costs energy. So the settled shared state tells apart states that differ by the photon's rotation, in the rule's sense, and by the same rule the photon becomes massive inside the metal. A magnetic field, carried by photons, then falls off inside the metal by the factor e over each length λ, the own length of a massive carrier: the penetration depth (Box 9.3). *The Coming of the Kinds*, Chapter 6, Section I, pictures the Higgs field's value as snow deepening over a field, through which walkers are slowed by how deeply they sink. The photon is a skier who glides over the snow and is not slowed at all; inside a superconductor the snow is of a kind the skier sinks in.

The photon's rotation, taken with four conditions that any law fixing the field from the charges must meet, also fixes the form of the laws of the electric and magnetic field. James Clerk Maxwell joined those laws into one account of the field in 1865, written then as twenty equations, and found from them that light is a wave of the field (Maxwell, 1865). They are written today as four laws, *Maxwell's four laws*, and Box 9.3 has used two of them as standard electromagnetism: Ampère's law, and the law that a magnetic field has no sources. Box 9.4 finds why all four laws have the form they have. The photon it follows is the carrier of the electric force in the atom and in light, the combination that stays massless because the Higgs field's value carries no electric charge.

Box 9.4. Why the field's laws have the form they have

Premises. (1) A charged wave's phase at one place, taken alone, is found by no measurement: a turn of the phase that differs from place to place, made together with a matching change of the potential, changes nothing that any measurement can find, and that matched pair of changes is the photon's rotation (this section; standard electromagnetism of charged waves). (2) A charged wave carried along a path has its phase turned by its charge divided by ħ, times the potential added up along the path; and in a matched pair of changes the potential changes so that its sum along any path changes by ħ divided by the charge, times the difference between the turns made at the path's two ends (standard electromagnetism; Chapter 10, Section II, uses the same rule). (3) In space and time together the potential has four parts at each place: the arrow of this section, with one part for each of the three directions of space, and the *electric potential*, whose difference between two places is the voltage between them (Chapter 1, Section II), as its part along time (standard electromagnetism). (4) The laws that fix the field from the charges act from each place on its neighbors, never at a distance, since nothing passes faster than light; they are the same for every observer in uniform motion; they hold the potential's rates of change in space and time up to the second rate, as the laws of motion hold a body's position up to its second rate of change, its acceleration; and they keep charge, which is never made or lost (standard physics). (5) The photon carries no charge, so the field is not its own source (Chapter 1, Section II).

Steps. Add up the potential round a small closed loop. By (2), a matched pair of changes alters that sum by ħ divided by the charge, times the difference between the turns made at the loop's two ends, and the two ends of a closed loop are one place, so the sum is the same whatever matched changes are made. By (1) and (2), a charged wave carried round the loop has its phase turned by its charge divided by ħ, times that sum, and a measurement can find that turn, as the shifted stripes of Chapter 10, Section II, show. So the sum round a small loop, for each unit of the loop's area, can be found; it is the field's part for the plane of that loop, and the

field is these parts taken together. A small loop in space and time lies in a plane of two directions, and space and time together have six such planes, one for each way of choosing two of their four directions, $4 \times 3/2 = 6$. Three of the planes are made of time and one direction of space, and three are made of two directions of space. So the field has six parts at each place. The three parts in planes of time and space are the electric field, and the three parts in planes of space are the magnetic field, whose part through a small loop in space is how much the potential turns round that loop, as this section found. How the six parts divide between the electric and the magnetic field depends on the observer's motion, since space and time mix between observers in uniform motion; so an electric field that moves past an observer is found as a magnetic field as well, as Chapter 1, Section VI, found inside the atom. Now take the sums round all the faces of any small closed box, each face's loop taken in the same sense as seen from outside the box. Together they add up to nothing, since each edge of the box is an edge of two faces and is passed once in each direction. For a box in space this is the first law: the magnetic field has no sources, so as much of it leaves any small region as enters it. For a box that spans an interval of time and two directions of space it is the second law: a magnetic field that changes in time drives an electric field round it, which is *Faraday's law of induction*. These two laws hold for any field built from one potential that has a value at every place of a region, whatever the charges do. The other two laws say how the charges shape the field. By the first steps the field can be found and the potential, taken alone, cannot, so these laws are written in the field. By (4) they hold the field's first rates of change and no higher, act from each place on its neighbors, and are the same for every observer in uniform motion; by (5) they are linear in the field. Under these conditions one form is left, with one number in it that the units of charge set, the magnetic constant μ_0 of Box 9.3: the way the field spreads out from each place equals μ_0 times the charge and the moving charge there; and this form keeps charge, as (4) requires (standard electromagnetism). Its part along time is *Gauss's law*: the electric field spreads out from charge. Its parts along space are the *Ampère-Maxwell law*: moving charge, together with an electric field that changes in time, drives a magnetic field round it. The four laws can also be found as the conditions under which one quant-

ity, the field's *action*, added up over space and time, is left unchanged by every small change of the potential (standard physics). The conditions above allow one further term in that quantity: the electric field times the magnetic field, each part of the one times the matching part of the other, added together. Added up over any region of space and time, that term depends only on the field at the region's boundary, so it changes none of the four laws (standard electromagnetism).

Result. Maxwell's four laws follow from the photon's rotation, a turn of a charged wave's phase made separately at each place with a matching change of the potential; from the four conditions of premise (4); and from a photon that carries no charge. Around a charge at rest they give a field that goes out alike in every direction and falls as the inverse square of the distance, which is Coulomb's law, as Volume One, Chapter 7, Section II, found from a massless photon that carries no charge, in three dimensions of space. For steady currents the fourth law is Ampère's law, as Box 9.3, premise (3), uses it, and the first law is the rule, used in the steps of Box 9.3, that a magnetic field has no sources. In empty space the four laws give changes of the field that travel at the speed $1/(\mu_0\varepsilon_0)^{1/2}$, which is c, since $\mu_0\varepsilon_0 = 1/c^2$ (Box 9.3, premise (4)). Maxwell found that speed so near the speed of light that he concluded that light is a wave of the field (Maxwell, 1865, Section 20), and Chapter 11 follows light into matter. The first two laws hold for any field built from a potential in this way. The second two are linear because the photon carries no charge, and so two beams of light pass through each other unchanged (Chapter 11, Section XI). Where the turn made separately at each place is a turn among several states, and not a turn of one phase, its carriers are themselves turned by it: in the zoo's words, “When a transformation has more than one way to act, its carriers are themselves acted on by it” (*The Story of the Particles*, Level 7, Section V). The laws of such a field are of the same kind as Maxwell's, and they are not linear (Yang and Mills, 1954); that is why the color field between two quarks gathers into a tube (Chapter 1, Section II).

The match goes further. In a condensate without charge, slow twists of the one phase are sound waves, as Section III found. In a superconductor the slow twists of the phase move charge. The electric push of the moved charge raises their least frequency from that of sound to the plasma frequency of Chapter 4, Section IX. The plasma frequency is the frequency at which a metal's free electrons swing back and forth together, set by the number of the electrons in each unit of volume, their charge and their mass. So the twists become the third way of turning, along its line of motion, that the photon takes up inside the metal. In the same way three of the Higgs field's four states become the third ways of turning of the W and Z bosons (Chapter 8, Section VIII; *The Coming of the Kinds*, Chapter 6, Chapter Overview). Philip Anderson drew that link from superconductors in 1963 (Anderson, 1963). *The Alphabet of Particles* records it in its entry for the Higgs boson: "Philip Anderson noted in 1963, from the physics of superconductors, that a massless carrier can gain mass when a field fills space". So the Meissner effect is the Higgs field's way of giving a carrier its mass, seen again in a metal: the shared state of pairs plays the settled value, and the photon plays the massive carrier.

The match is in how the carrier gains its mass. The metal keeps its own sharp transition temperature. Below T_c the whole turns of its one phase round a ring can be measured, as the current they carry (Section IX), and above T_c there are none. So a difference that can be measured separates the two arrangements, as the magnet's direction separates its two (Chapter 8, Section V). The Higgs field's settling has no such measurable difference between the settled field and the unsettled one, and it is the crossover that Chapter 8, Section VIII, found.

So we now know why a superconductor keeps a magnetic field out. Its phase is one across the metal and is measured only together with the field's potential, so a field inside would wind the potential, and the pairs, unable to wind their phase to match, would move. The shared state answers with currents at its surface, and the field reaches in only the penetration depth, $\lambda = (m_e/(\mu_0 n e^2))^{1/2}$ for every electron sharing the phase.

Seen through the rule of *The Coming of the Kinds*, the shared state of charged pairs tells apart the states the photon rotates among, so the photon gains a mass inside the metal, and the penetration depth is its reach.

XII. Threads of Field

Push the floating magnet of Section XI sideways, and with some superconducting disks it slides back to where it was. With others it stays where it is put, and turned over, the disk holds the magnet hanging beneath it. A disk that holds the magnet where it is put cannot be keeping the field wholly out. Where does the field go in?

Section XI found that a field inside a superconductor would wind the potential round a loop, and that the pairs, unable to wind their phase to match, would move. That holds wherever the phase is one and does not wind. The phase can wind round a thread at whose center the shared state is missing, as the condensate of Section IV winds round a vortex. Round such a thread the phase can wind as the potential winds, matching it, so that far from the thread the pairs stay at rest. So the field can enter a superconductor along threads where pairing is broken, with the phase winding whole turns round each.

Each thread carries a fixed amount of field. Far from a thread, where its whirl of current has died away, the speed of the pairs is zero. So by Box 9.3, premise (2), the rate at which the phase changes from place to place equals the pairs' charge, 2e, times the potential, divided by ħ. Round a loop the phase winds a whole number of turns, $n \times 2\pi$. The sum of the potential round a loop is the field passing through the loop, its *magnetic flux*, the field times the area it passes through, counted in *webers*, one tesla through one square meter. So the flux through any loop round a thread is $n \times 2\pi\hbar/(2e) = n\ h/(2e)$. A thread round which the phase winds once carries one *flux quantum*, $h/2e = 2.067833848 \times 10^{-15}$ webers, exact since the Planck constant and the electron's charge are fixed by definition

(CODATA 2022). In a field of one tesla the threads stand about 49 nanometers apart, in a triangular array (computed). Alexei Abrikosov found this state of threads in 1957 (Abrikosov, 1957), and the threads, made visible by fine magnetic powder settling where each meets the surface, stand in the regular array he found (Essmann and Träuble, 1967). Chapter 10 counts the flux in its whole units exactly, and finds what the factor two in h/2e fixes.

Whether a superconductor lets a field in as threads or keeps it out entirely is set by two lengths. One is the penetration depth λ, over which the field can change. The other is the coherence length, the size of a pair, over which the shared state can change. At a boundary between a region holding field and a region of shared state, the pairing falls to nothing over the coherence length, and the field dies away over the penetration depth. Where the coherence length is the longer, a band at the boundary has lost its pairing, which costs energy, while the field has already died away there, so nothing is saved in return: the boundary costs energy. Where the penetration depth is the longer, the field reaches into a band where the pairs are already whole. There the saving of field energy is larger than the cost of the lost pairing, and the boundary lowers the energy (Ginzburg and Landau, 1950; Abrikosov, 1957). So where the pairs are large against the penetration depth, threads do not pay, and the superconductor keeps the field wholly out until a field strong enough, its *critical field*, breaks the shared state throughout: a *type I superconductor*. Where the pairs are small against the penetration depth, the field enters as threads above a lower critical field, more and more of them as the field grows, until at an upper critical field their cores fill the metal: a *type II superconductor*. The dividing line is where the ratio of the penetration depth to the coherence length, the *Ginzburg-Landau parameter*, is one over the square root of two (Ginzburg and Landau, 1950; Abrikosov, 1957). Aluminum, tin and lead are of type I, with critical fields of 0.01, 0.03 and 0.08 tesla. Niobium is of type II, and alloys made for magnets are of type II with upper critical fields far higher: about 15 tesla for niobium-titanium and 30 tesla for niobium-tin (standard tables of superconductors).

The threads explain the magnet that stays where it is put. A current through a type II superconductor pushes sideways on its threads, and a thread that moves drags its core of broken pairs through the metal, which takes energy and makes resistance. Flaws in the metal hold the threads in place, as the flaws of Chapter 8, Section VII, hold the walls between domains. So a type II superconductor carries current with no resistance up to a *critical current*, the current at which the push on the threads tears them from the flaws. Makers of superconducting wire build flaws into it on purpose to hold the threads, and a disk that holds a magnet where it is put does so because the threads of the magnet's field are held in the disk.

Since 1986 superconductors have been found far above the temperatures of the metals of Section VI. Georg Bednorz and Alex Müller found that a ceramic of lanthanum, barium, copper and oxygen becomes a superconductor near 35 kelvin (Bednorz and Müller, 1986). In 1987 Paul Chu and his colleagues made a ceramic of yttrium, barium, copper and oxygen that reached 92 kelvin, above the 77 kelvin at which liquid nitrogen boils, which made it a superconductor that cheap liquid nitrogen can cool. Copper oxides containing mercury have passed 130 kelvin at ordinary pressure (standard tables of superconductors). These *cuprates*, ceramics built of layers of copper and oxygen, are type II superconductors, and their pairs carry the charge 2e, as the flux quantum h/2e measured in them shows (Gough et al., 1987). Other families have followed: magnesium diboride at 39 kelvin (Nagamatsu et al., 2001), materials of iron and arsenic from 2008, the first at 26 kelvin (Kamihara et al., 2008), and hydrogen sulfide squeezed to 155 billion pascals at 203 kelvin (Drozdov et al., 2015). Cooper's argument of Box 9.2 needs only that some attraction act between electrons near the Fermi level, whatever its source. In squeezed hydrogen sulfide the source is the pull through the lattice of Section VI: made with deuterium in place of hydrogen, it becomes a superconductor at a lower temperature, the isotope effect of Section X (Drozdov et al., 2015). Each family's transition temperature is a measured value.

So we now know where a magnetic field goes into a superconductor. In a type I superconductor it stays out until the critical field destroys the shared state. In a type II superconductor it enters as threads round which the phase winds whole turns, each carrying one flux quantum, h/2e, because each pair carries the charge 2e. Flaws that hold the threads let a type II superconductor carry large currents in strong fields.

XIII. The Pair's Charge, and What Is Counted

Shoes are sold in pairs, and a shop that sells only whole boxes of shoes always sells an even number of shoes, whatever else changes. A superconductor's charge moves in pairs. What does that fix?

A Cooper pair is two electrons, each of one unit of charge, so the pair carries two units, 2e, and the shared state built of pairs carries charge in units of two. That factor two is a count, fixed by the structure of the pair, and it is the same in every superconductor of every kind. It showed itself in 1961, when Bascom Deaver and William Fairbank, and Robert Doll and Martin Näbauer, cooled small superconducting cylinders in a magnetic field (Deaver and Fairbank, 1961; Doll and Näbauer, 1961). They found the flux trapped in them only in whole numbers of units of h/2e, the smallest trapped flux being h/2e and not h/e: the charge whose phase winds round the cylinder is 2e.

Two kinds of number have appeared in this chapter, and they stand differently. The pair's two units of charge and the whole turns of the phase round a loop, which make the flow of a condensate come in units of h/m and the flux of a thread in units of h/2e, are counts: how many electrons in a pair, how many turns of the phase round a loop. They are fixed by structure, by the evenness that lets a pair share a state and by the one phase that must come back to itself, and no material can change them. The transition temperatures, the gaps, the penetration depths and coherence

lengths, the 2.17 kelvin of helium-4 and the 1043 kelvin of iron's Curie point are values of measures, set by the strengths of the pulls and pushes in each material, and they are measured.

So we now know what the pairs fix. Each pair carries the charge 2e, the shared state carries charge in units of two, and a superconducting ring traps flux in units of h/2e. The charge 2e of each pair, the units of two in which the shared state carries charge, and the flux quantum h/2e are counts fixed by structure, the same in every superconductor. The measured values set beside those counts differ from one material to the next.

In Use

The magnet of a hospital's scanner for magnetic resonance imaging is a superconductor at work. Its coil is wound of niobium-titanium wire, a type II superconductor held in liquid helium, and most such magnets make a field of 1.5 tesla, with stronger ones at 3 tesla. Most clinical scanners use such magnets, cooled by liquid helium, and around 50,000 scanners are in use in the world (standard accounts of medical imaging). Once its current has been set, the coil is closed on itself and needs no power supply. The current goes round as the current in the lead ring of Section I does, a twist of one phase that can lessen only by a slip of whole turns (Section IX). The field stays steady enough for the scanner to read the faint signals of the nuclei of the body's hydrogen, which Chapter 12 takes up. A copper coil making the same field would turn its whole current's power into heat in its resistance; the superconducting coil turns none, and needs only to be kept cold.

The largest machine built for physics is held on course by superconductors. The Large Hadron Collider at CERN, the European laboratory for particle physics near Geneva, bends its two beams of protons round a ring 27 kilometers long. It bends them with 1,232 dipole magnets, magnets each with one north and one south pole that turn the beam's path, wound of niobium-titanium wire clad in copper, whose field rises to 7.7 tesla. The

magnets are kept at 1.9 kelvin by 96 tonnes of superfluid helium-4 (standard accounts of the Large Hadron Collider). The superfluid is chosen for more than its cold. Below 2.17 kelvin helium-4 carries heat away by the counterflow of its two parts, the normal part moving out from a warm spot as the superfluid part moves in (Section III), far faster than any ordinary liquid carries heat. And it seeps through the narrowest gaps in the windings, so the whole length of wire stays cold.

Cables can be made of superconducting tape. A tape coated with a cuprate of yttrium, barium, copper and oxygen carries more than 500 amperes for each centimeter of its width at 77 kelvin, the temperature of liquid nitrogen, which is cheap and plentiful (standard accounts of superconducting wire). A cable of such tape carries power with no loss in the conductor itself, needing only its cooling, and many times the current of a copper cable of the same size.

Liquid helium makes the cold for all of these. Helium-4 boils at 4.2 kelvin at the pressure of the air, and it stays liquid at that pressure down to absolute zero, as its rare isotope helium-3 does and no other substance does. It is drawn from natural gas, which can hold up to seven percent helium, by cooling the other gases out of it until helium alone is left (standard accounts of liquid helium). Every superconducting magnet that cannot be cooled by liquid nitrogen rests on that supply, and the same liquid, cooled below 2.17 kelvin, is the superfluid with which this chapter began.

Summary

Wholes made of an even number of particles of spin one half are not excluded. So, crowded and cold, they gather into the lowest state below the temperature at which their thermal wavelength reaches their spacing (Box 9.1). A large share of the gathering is then in one state, and the gathering is a condensate, with one amplitude and one phase across the whole of it. Wholes made of an odd number are excluded and cannot gather singly. That one rule determines both the condensation and the difference

between the two heliums. Helium-4, six particles of spin one half, becomes a superfluid at 2.17 kelvin. Helium-3, five, becomes one only when two of its atoms pair, below about a thousandth of a kelvin, 0.93 thousandths at zero pressure and 2.5 thousandths at the melting pressure, its pairs with aligned spins.

A condensate flows without friction because slowing it means lifting part of it into an excitation, and a flow slower than the least ratio of energy to momentum among the excitations cannot make one. When the wholes push one another, the lowest excitations are sound waves, so that ratio is above zero, at the speed of sound or, in helium-4, at the rotons' lower ratio. Wholes that did not push would have no safe speed. Because the phase is one, the flow round any loop is a whole number of units h/m, and a spinning superfluid fills with vortex threads of one turn each.

In a metal the slow, heavy lattice turns the electrons' screened push into a slight pull between electrons near the Fermi level. Two electrons just above the filled states bind under any pull however small, because they have nothing lower to fall to (Box 9.2). The pairs, even wholes, share one phase across the metal, and breaking one costs at least twice the gap, about 3.5 times kT_c. A current is a twist of the one phase, a form of the shared state and not a state above it, which can lessen only by the phase slipping a whole turn. So a steady current meets zero resistance at every temperature below the transition, though heat breaks some pairs, and the metal resists as before above it. Heavier nuclei vibrate more slowly and narrow the band in which the pull acts while leaving its strength the same, so the transition falls as one over the square root of the nuclear mass. Superconductivity depends on the mass of the nucleus, which Chapter 12 follows further. Because the phase is measured only together with the field's potential, the shared state keeps a magnetic field out except in the penetration depth (Box 9.3). The same matched turning of the phase and the potential, with four conditions on any law that fixes the field from the charges and a photon that carries no charge, gives Maxwell's four laws of the electric and magnetic field, for the photon of the atom and of light (Box 9.4). In the rule of *The Coming of the Kinds*, the

shared state of charged pairs tells apart the states the photon rotates among, so the photon gains a mass inside the metal, and the penetration depth is its reach. The photon's gaining a mass inside the metal is the Higgs field's way of giving a carrier a mass, seen again in a metal. In type II superconductors the field enters as threads, each carrying one flux quantum h/2e, because each pair carries the charge 2e.

The counts these results rest on, the evenness of the wholes, the pair's two units of charge and the whole turns of the phase, are the same in every condensate and every superconductor. The transition temperatures, gaps and lengths are measured values of each. Chapters 8 and 9 have found two kinds of order among many. When cold, a crystal may pick one direction for its spins, held by all of them, as a magnet does, findable and so lost at a sharp point. Or wholes that are not excluded may gather into one phase, as the superfluids and superconductors do. The Higgs field shares the magnet's structure without its findable pick, and it shows its rule for giving a carrier mass most nearly in the superconductor, where the photon gains a mass.

The pairs' phase must come back to itself round every loop, and round a superconducting ring it traps flux only in units of h/2e. One phase that must return to itself counts in whole numbers. What does it count exactly?

✶

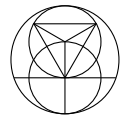
KEY CONCEPTS

- **Fermi sea; Fermi level.** The filled states of fermions at the lowest temperature, and the energy of the top of them.
- **Bose-Einstein condensation.** The gathering of a large share of bosons, or of wholes made of an even number of fermions, into the one lowest state, below the temperature at which their thermal wavelength reaches about their spacing (Box 9.1).
- **Amplitude; phase.** The height of a particle's wave at each place; the chance of finding the particle there grows as its square; and the stage of a wave's swing at a place, counted as a fraction of a whole turn.

- **Condensate.** A gathering of many wholes into one state, with one amplitude and one phase across the whole of it; the share of its wholes in the lowest state of one whole's motion is one measure of it, nearly all of them in a thin gas and about eight percent in liquid helium-4.
- **Excitation; Landau critical velocity.** A definite amount of energy, with a definite momentum, lifted out of a condensate; the least ratio of energy to momentum among the excitations, below which a flow can make none and so loses nothing.
- **Phonons and rotons.** The quanta of sound in superfluid helium; and the excitations near the least energy that helium's excitations reach at wavelengths about the spacing of its atoms.
- **Superfluid; two-fluid model; second sound.** A liquid that flows without friction because a large share of it is one state; its account as a frictionless superfluid part and a normal part of excitations carrying all the entropy; a wave of temperature in which the two parts move against each other.
- **Quantized vortex.** A thread at whose center the condensate is missing, round which the phase winds whole turns; the flow round it is a whole number of units h/m.
- **Isotope; helium-4; helium-3.** Different forms of one element, with the same number of protons and different numbers of neutrons; helium of two protons and two neutrons, six particles of spin one half with its electrons; and helium of two protons and one neutron, five.
- **Superconductor; transition temperature; superconductivity.** A solid that below its transition temperature, T_c, carries a steady current with zero resistance and keeps a magnetic field out of itself.
- **Debye temperature.** The temperature Θ at which $k\Theta$ equals the quantum of a crystal's highest mode.
- **Bargmann's bound.** A pull of short reach binds two particles only when its strength passes a threshold, because confinement costs energy.

- **Cooper pair.** Two electrons just above a filled Fermi sea bound by any attraction however small, because they have nothing lower to fall to; an even whole (Box 9.2).
- **BCS theory; energy gap; coherence length.** The account of superconductivity of Bardeen, Cooper and Schrieffer; the least energy needed to free one electron from the shared state of pairs, about 1.76 kT_c; and the size of a pair.
- **Isotope effect.** The fall of a metal's transition temperature, as one over the square root of the nuclear mass, when it is made of heavier isotopes.
- **Potential; curl.** An arrow at each place from which the magnetic field follows, the field through a small loop being how much the potential turns round that loop; and the curl, how much a quantity turns round a small loop at a place, for each unit of the loop's area.
- **Maxwell's four laws; Faraday's law of induction; Gauss's law; Ampère-Maxwell law.** The laws of the electric and magnetic field: a magnetic field has no sources; a magnetic field that changes in time drives an electric field round it; the electric field spreads out from charge; and moving charge, together with an electric field that changes in time, drives a magnetic field round it. The first two hold for any field built from a potential, and the last two are linear because the photon carries no charge (Box 9.4).
- **Electric potential; action.** The part along time of the field's potential in space and time, whose difference between two places is the voltage between them; and the quantity, added up over space and time, that every small change of the potential leaves unchanged when the field's laws hold (Box 9.4).
- **Meissner effect; penetration depth.** A superconductor's pushing of a magnetic field out of itself; and the depth, $\lambda = (m_e/(\mu_0 n e^2))^{1/2}$ for every electron sharing the phase, over which the field reaching in falls by the factor e (Box 9.3).

- **Own length.** $\hbar/(mc)$, the length that a carrier's mass, $\hbar$ and c make together; inside a superconductor the photon's own length is the penetration depth.
- **Magnetic flux; weber; flux quantum.** The field times the area it passes through, in webers, one tesla through one square meter; and $h/2e = 2.067833848 \times 10^{-15}$ webers, the flux of one thread round which the pairs' phase winds once.
- **Type I and type II superconductors; critical field; Ginzburg-Landau parameter.** Superconductors that keep a field wholly out until a critical field destroys the shared state; and those that let it in as threads between a lower and an upper critical field; the two are divided by the ratio of the penetration depth to the coherence length, at one over the square root of two.
- **Critical current.** The current at which the push on a type II superconductor's threads tears them from the flaws that hold them, and resistance begins.
- **Cuprates.** Ceramic superconductors built of layers of copper and oxygen, with transition temperatures from 35 kelvin to above 130 kelvin.



Chapter 10

Steps Kept Exactly

CHAPTER OVERVIEW

A chip of superconducting junctions gives the volt, and a sheet of electrons in a magnet gives the ohm, the same in every laboratory and every material to ten decimal places. In this chapter we find why. From one phase that must return to itself, a pair that carries two units of charge, and a winding that no smooth change can alter, matter keeps numbers exactly. Carried round a loop, a charge's phase turns by its charge times the magnetic flux through the loop, divided by $\hbar$ (the Aharonov-Bohm phase). The pairs' phase in a superconducting ring must come back to itself, so the flux through the ring is a whole number of flux quanta, $h/2e$ (Box 10.1): the two is the pair's, and the whole number is the ring's. Where two superconductors meet across a thin barrier, a Josephson junction, pairs cross by the difference of the two superconductors' phases. A current flows with no voltage, $I = I_c \sin \delta$, and a voltage V makes the current swing at the frequency $2eV/h$, in a ratio the same in every material because nothing but 2e and h enters it. Electrons held to a sheet in a strong field take energies only in separate levels, Landau levels, each of which has one state for each flux quantum h/e. Where the filled levels end in a gap, the sheet carries current across a voltage and none along it. The ratio of the voltage across the sheet to the current along it, its Hall resistance, is then $h/(\nu e^2)$, ν a whole number, held flat over a range of field by the flaws that trap states between the levels. These plateaus are exact because the Hall conductance, the Hall resistance turned upside

down, is a winding: a whole number of turns of the filled states' phases, the Chern number, which no flaw, shape or material that keeps the gap can change (Box 10.2). Where electrons push hard in a partly filled level, they take states at fractions of the level. For single electrons of one kind in one layer, exchange reverses the sign of their state, so the simplest fractions have odd denominators. An even denominator needs something exchange does not reverse: pairs, as at 5/2, or two layers. The fractional charges are collective excitations of the gathering of electrons. Crystals whose bands wind carry states on their edges or surfaces. A whole-number winding needs time reversal broken, time reversal being the running of every motion backward. The topological insulators keep time reversal and carry a two-valued index instead, because reversing time twice reverses an electron's state, and their boundary states come in partners of opposite spin moving opposite ways. The Planck constant and the electron's charge are values; the factors by which they enter, the two of the pair and the whole numbers, are fixed by structure. So the ratios $2e/h$ and h/e^2 come out the same in every material, and they are exact in the units defined since 2019. Set against the impedance of empty space, a constant of empty space measured in ohms, h/e^2 gives the fine-structure constant: $R_K/Z_0 = 1/(2\alpha)$.

I. A Constant Read from a Chip

Chapter 9 ended with a question: one phase that must return to itself counts in whole numbers, so what does it count exactly?

In a national laboratory of measurement, a chip the size of a fingernail sits in liquid helium at about 4 kelvin. A cable feeds it microwaves at a frequency read from an atomic clock, a clock that counts the swings of the light that atoms of one kind give out or take up (Chapter 12, Section XV), and across its two ends a steady voltage appears. The laboratory takes that voltage as its volt. In the next room a small square of gallium arsenide, a semiconductor, or of graphene, a sheet of carbon one atom thick, sits in a strong magnet at a few kelvin. A current is passed along the square,

the voltage across it is read, and the ratio of the two is 25,812.807 ohms, or exactly a half, a third or a quarter of that. Laboratories in different countries, with chips made of different metals in different ways, find the same voltage for the same frequency. Compared with a standard carried from one to the other, they agree to better than a part in a billion (standard accounts of the Josephson voltage standard). Sheets of gallium arsenide and of graphene give the same resistance to within about one part in ten billion (Janssen et al., 2012).

Every other property this volume has measured differs from one material to the next. Chapter 9, Section XIII, showed that a superconductor's transition temperature, its gap and its penetration depth are values that differ from one material to the next. The resistance of a copper wire depends on how pure it is and how warm (Chapter 6, Section VIII). Yet here a piece of matter, cold, gives a number that is the same in every sample, to ten decimal places. So the reader's question is this: how can a material measure a constant of nature to ten decimal places?

The answer rests on eight results, each already found or standard. They are gathered here so that we can point back to them in later sections, and each is named with the sections that use it. The first of the eight results is that a particle's wave gives one amplitude for each place, the amplitude being the height of the wave at that place. The chance of finding the particle at a place grows as the square of the amplitude there (Chapter 9, Section II). And a place reached again by going round a loop is not told apart by any comparison from the place that was left. By the principle of identity, in the words of *The Quantum Passage*, Chapter 8, Section VI, "what no comparison can distinguish, in any way at all, even in principle, is one thing and not two" (Chapter 1, Section IV). So the place reached again is the same place, with the same amplitude. The phase of a wave, the stage of its swing at a place counted as a fraction of a whole turn (Chapter 6, Section II), can therefore change round a closed loop only by a whole number of turns. Sections III, V and VII use this first result. The second of the eight results is the rule by which a magnetic field acts on the phase of a wave, and Section II uses the rule first. Carried round a loop, a charged

particle's phase turns by the particle's charge times the magnetic flux through the loop, divided by ħ. Here ħ is the reduced Planck constant, Planck's constant h divided by 2π, 1.054571817... × 10^{-34} joule seconds (Chapter 1, Section II). The third of the eight results is that a state of definite energy E keeps its form in time while the state's phase advances at the rate E/ħ (standard quantum mechanics; Chapter 6, Section VIII, uses the same fact). Section IV uses the third result. The fourth is that exchanging two fermions of one kind reverses the sign of their joint state (Chapter 1, Box 1.2), a fermion being a particle whose spin is an odd number of halves, such as the electron, whose spin is one half; Section VIII uses it. The fifth is that a whole number does not change under any smooth change, since a smooth change can move it only by a small amount and a whole number has no small amounts to move by (mathematics); Sections VII and IX use it. The sixth is that the electron states of a crystal are labeled by their crystal momentum, ħk, a point of the Brillouin zone, the single cell of momenta that Chapter 6, Section II, showed to hold every state of a band once; Section VII uses it. The seventh is time reversal: the laws of electromagnetism run equally well backward, with every motion reversed, so long as no magnetic field is applied from outside (standard physics); Section IX uses it. And the eighth is that a particle of spin one half returns to its starting state only after two full turns, as the belt with a buckle does, while one turn reverses its sign (Chapter 1, Section V, from *The Kinds of Particle*, Chapter 1, Section VIII); Section IX uses it.

II. A Charge's Phase Round a Loop

In 1986 Akira Tonomura and his colleagues at Hitachi made a ring magnet a few micrometers across, a doughnut of magnetic metal whose field runs round inside the ring and nowhere else. They sealed it in a layer of superconducting metal, which keeps any field from leaking out, and a layer of copper over that. They sent a beam of electrons at it, part of each electron's wave passing through the hole of the ring and part passing outside.

They let the two parts meet beyond the ring, where their waves make a pattern of light and dark stripes, as two sets of overlapping waves do. No electron passed through any magnetic field: the field was sealed inside the ring. Yet the stripes were shifted by the field inside the ring (Tonomura et al., 1986). How can a magnetic field act on an electron that never passes through it?

A magnetic field acts on a charged wave through the field's potential, an arrow at each place from which the magnetic field follows: the field through a small loop is how much the potential turns round that loop (Chapter 9, Section XI). Outside the ring magnet the field is zero, but the potential is not. Added up round any loop that encircles the ring, the potential gives the field passing through the loop, its magnetic flux, the field times the area it passes through, counted in webers, one tesla through one square meter (Chapter 9, Section XII). A tesla is the unit of magnetic field, the field being the push and pull that moving charges and magnets exert on other moving charges and magnets at each place around them (Chapter 8, Section II). Chapter 9, Section XI, showed that the phase of a charged wave is measured only together with that potential. The rule that goes with it is standard: a particle of charge q carried along a path has its phase turned by $q/\hbar$ times the potential added up along the path. So carried once round a closed loop, its phase turns by $q/\hbar$ times the magnetic flux through the loop (Aharonov and Bohm, 1959). That turning is the *Aharonov-Bohm phase*, named for Yakir Aharonov and David Bohm, who stated it in 1959, after Werner Ehrenberg and Raymond Siday had found it in 1949 (Ehrenberg and Siday, 1949).

The two parts of an electron's wave, one passing on each side of the ring, together make a loop round the ring magnet. They meet with their phases differing by $e\Phi/\hbar$, with e the size of the electron's charge and Φ, read "phi", the flux sealed in the ring. So the stripes they make are shifted by that much, though neither part met any field. In Tonomura's ring the superconducting layer had a further effect, which Section III describes: it

trapped the magnet's flux only in whole units of h/2e. So the shift of the stripes came out either none or exactly half a stripe, as the rule requires for flux in those units (Tonomura et al., 1986).

So we now know how a magnetic field acts on a charge that does not pass through it. The field's potential reaches where the field does not, and carried round a loop, a charge's phase turns by its charge times the flux through the loop, divided by ħ. With the first result of Section I, that the phase can change round a loop only by whole turns, this rule is all the next section needs.

III. Flux in Whole Units

In Volume One, Chapter 1, Section V, we watched the minute hand of a clock: in one hour it makes one whole turn and stands exactly where it began, so the angle it sweeps in any number of hours is a whole number of turns. An angle that must come back to itself counts in whole turns. Chapter 9, Section XII, showed that a thread of magnetic field in a superconductor carries the flux h/2e because the pairs' phase winds once round it. Now take a whole ring of superconducting metal, cool it in a magnetic field, and take the field away. The ring keeps a field threading its hole, held there by a current that runs round the ring's inner surface. How much flux can such a ring hold?

A superconductor is a solid that below its transition temperature carries a steady current with zero resistance and keeps a magnetic field out of itself (Chapter 9, Section VI). Its electrons are bound in Cooper pairs, two electrons bound by a slight attraction, which share one state with one amplitude and one phase across the whole metal (Chapter 9, Sections VII and VIII). Each pair carries two units of charge, 2e (Chapter 9, Section XIII). The ring's phase, carried once round the ring, must come back to itself, so it turns by a whole number of turns. And by the rule of Section II, the potential of the flux through the hole turns the pairs' phase as it goes round. In Box 10.1 we put the two together.

Box 10.1. The ring counts whole flux quanta

Premises. (1) The Cooper pairs of a superconductor share one state with one phase across the metal, and each pair has charge 2e (Chapter 9, Sections VIII and XIII). (2) Carried round any closed loop inside the metal, that phase changes by a whole number of turns, $n \times 2\pi$, with n a whole number, zero included (Section I). (3) A particle of charge q moves with the speed ($\hbar$ times the rate at which its phase changes from place to place, less q times the potential A) divided by its mass (Chapter 9, Box 9.3, premise 2); added up round a closed loop, the potential gives the magnetic flux Φ through the loop (Section II). (4) Inside a superconductor, deeper than a few penetration depths below its surface, no current flows (Chapter 9, Box 9.3).

Steps. Take a loop that runs round the ring through the inside of its metal, everywhere many penetration depths from every surface. By (4) the pairs on that loop do not move, so by (3), with $q = 2e$, at every point of the loop the phase changes from place to place at the rate $2eA/\hbar$. Adding these changes round the loop, the phase changes in all by $(2e/\hbar)$ times the potential added up round the loop, which is $2e\Phi/\hbar$. By (2) this total is $n \times 2\pi$. So $\Phi = n \times 2\pi\hbar/(2e) = n\,h/(2e)$.

Result. The flux through a superconducting ring is a whole number of flux quanta, $\Phi = n\,h/2e$, with $h/2e = 2.067833848 \times 10^{-15}$ webers, exact since the Planck constant and the electron's charge are fixed by definition (CODATA 2022). The two in the unit is the pair's, and the whole number is the ring's.

Two counts enter the result, and each has its own source. The two in h/2e is the pair's: a ring whose carriers of charge were single electrons would count its flux in units of h/e. Bascom Deaver and William Fairbank, and Robert Doll and Martin Näbauer, found in 1961 that superconducting cylinders hold flux in units half that size, as Chapter 9, Section XIII, describes (Deaver and Fairbank, 1961; Doll and Näbauer, 1961). The whole number is the ring's: it says how many turns the phase makes round the

ring, and only the phase's need to come back to itself sets it. Neither count depends on the ring's metal, its size, its shape or its temperature below the transition.

The unit is small. One flux quantum through a ring of one square millimeter is a field of two billionths of a tesla (computed). The Earth's field of about fifty millionths of a tesla, passing through a ring of one square centimeter, is about two and a half million flux quanta (computed). A ring cooled in the Earth's field traps the whole number nearest to what passed through it when it became a superconductor. It then keeps that number exactly while it stays cold, since to change it the phase would have to slip a whole turn across the whole ring (Chapter 9, Section IX). So the flux through a superconducting ring is always a whole number of units of h/2e, zero included, and is never counted in any smaller unit.

So we now know what a superconducting ring counts exactly. Its pairs' one phase must come back to itself round the ring, and the flux through the ring turns that phase by $2e\Phi/\hbar$, so the flux is a whole number of flux quanta, h/2e. The two is the pair's, and the whole number is the ring's.

IV. Two Superconductors and a Thin Barrier

Two cars wait side by side at a red light, each blinking to turn. Their blinkers flash at nearly the same rate, and for a while they flash together. Then one draws ahead, and they flash in turn, and then they come back together again. The two flash together once more each time the faster blinker has gained one whole flash on the slower, so the rhythm of their falling into and out of step is the difference of their two rates. What happens when two superconductors, each with its own phase, are set side by side?

Join two pieces of superconductor through a thin layer that is not superconducting, usually an insulator about a nanometer thick. The arrangement is a *Josephson junction*, named for Brian Josephson, who found in 1962 what it does (Josephson, 1962). Each piece has its own shared

state of pairs, with its own phase, and the pairs can pass through the thin layer by tunneling, the passing through a barrier of Chapter 3, Section III. Josephson found that the current of pairs through the layer is set by the difference between the two phases, δ, read "delta": $I = I_c \sin \delta$ (Josephson, 1962). Here I_c is the largest current the junction can pass this way, the junction's critical current, a second use of the name apart from the critical current of a wire in Chapter 9, Section XII. The sine of an angle, $\sin \delta$, is 0 at no turn, rises to 1 at a quarter turn, falls to 0 at a half turn and to -1 at three quarters, and comes back to 0 at a whole turn. The form follows from what the current must do, in three conditions. It must be the same when the difference of phase is changed by a whole turn, since a whole turn of the phase changes nothing that any measurement can find. It must be zero when the two phases are equal, since then nothing tells one direction across the layer from the other. And it must reverse when the difference reverses. The sine is the simplest form that meets all three, and other forms that meet them add terms that swing two, three or more times for each whole turn of δ. Those further terms come from pairs crossing the layer two or more at a time, and a thin insulating layer lets pairs through so rarely that such crossings are far rarer still: for such a barrier the sine is the whole of it (Josephson, 1962).

Two results follow, one for a junction with no voltage across it and one for a junction with a voltage. With no voltage, the two phases keep a fixed difference, and a steady current flows through the insulating layer, any current up to I_c, with no voltage at all. A steady current through the insulating layer with no voltage is the *DC Josephson effect*, DC standing for direct current, a current that flows steadily one way. Philip Anderson and John Rowell saw the DC Josephson effect in 1963 (Anderson and Rowell, 1963). With a steady voltage V across the junction, a pair on one side has the energy 2eV more than a pair on the other. A state of definite energy E has its phase advance at the rate $E/\hbar$ (Section I), so the two phases advance at rates that differ by $2eV/\hbar$, and their difference δ grows steadily, as the two blinkers drift in and out of step. The current $I_c \sin \delta$ then swings

back and forth at the frequency f = 2eV/h. A swinging current across the junction under a steady voltage is the *AC Josephson effect*, AC standing for alternating current, a current that swings back and forth. The ratio of frequency to voltage is 2e/h, the *Josephson constant*, 483,597.8484 billion swings each second for each volt (computed from the exact h and e). So even a millionth of a volt sets the current swinging 483.6 million times each second, a frequency that a clock can count.

That ratio is the same in every junction, of whatever superconductor, whatever its barrier and whatever its size, because nothing enters it but the pair's charge 2e and the Planck constant h. The pair's two units of charge are a count, and the rule that a state's energy sets the rate at which its phase advances holds for every state. Measured, junctions of different superconductors give the same ratio to within two parts in 10^{16} (Tsai, Jain and Lukens, 1983).

Run backward, the junction turns a frequency into a voltage. Shine microwaves of frequency f on a junction, and as the current through it is raised, the voltage across it climbs in flat steps, at the voltages n hf/2e with n a whole number (Shapiro, 1963). On each step the junction's own swinging locks to the microwaves. For microwaves of 75 billion swings each second each step is 155 millionths of a volt (computed). A chip of some twenty thousand junctions in series, each on its step, gives ten volts that depend only on the frequency, which a clock reads to far better than a part in a billion (standard accounts of the Josephson voltage standard). That chip is the one in liquid helium of Section I.

Two junctions set in one superconducting ring make a magnetometer, a meter of magnetic field, of extreme delicacy. The largest current the ring can pass with no voltage rises and falls as the flux through the ring changes, once for each flux quantum h/2e (Jaklevic, Lambe, Silver and Mercereau, 1964). It does so because the flux shifts the two junctions' phase differences against each other, by the rule of Section II. A ring of a square centimeter meets one flux quantum in a field of two hundred-billionths of a tesla. By measuring a small fraction of one quantum, such a

device, a *SQUID*, from superconducting quantum interference device, reads fields as small as a few millionths of a billionth of a tesla when it averages for one second (standard accounts of SQUIDs).

So we now know what happens where two superconductors meet across a thin barrier. Pairs cross by the difference of the two superconductors' phases, so a current flows with no voltage up to the junction's critical current. A voltage V makes the phases drift apart at $2eV/\hbar$, so the current swings at the frequency $2eV/h$ in every material, and microwaves turn back into voltages of exactly $hf/2e$ for each step.

V. Electrons in a Sheet, in a Strong Field

Old photographs of a bubble chamber, a tank of liquid in which charged particles leave trails of tiny bubbles, show the trails curling into circles and spirals. The chamber sat in a magnet, and the magnet's field pushed each charged particle sideways, at right angles to its motion, so that it went round in a circle. The slower ones curled the tightest. Chapter 6, Section VII, showed the same sideways push at work in the Hall effect, where a magnetic field across a current crowds the carriers to one edge of a strip. What states can electrons take when they are held to a thin sheet and a strong field passes through it?

Electrons can be held to a sheet. Where a crystal of gallium arsenide meets a crystal of gallium arsenide with some aluminum in it, the electrons given up by added atoms gather in a thin layer at the boundary, free to move along it and unable to move across it. The channel of a field-effect transistor, under its gate, holds its electrons the same way (Chapter 7, Section V). Such a layer is called a *two-dimensional electron gas*: a sheet of electrons free to move in its two directions and held in the third.

In a magnetic field B across the sheet, an electron of speed v feels the sideways force evB, which turns it round a circle of radius r with $mv^2/r = evB$, so $v/r = eB/m$ (standard electromagnetism). So it goes round at the angular frequency $\omega_c = eB/m$, read "omega c", the same for every speed,

since a faster electron goes round a larger circle in the same time. In a crystal m is the band's effective mass, the mass with which an electron in a band answers a push, set by the band's curvature (Chapter 6, Section VII), 0.067 of the electron's mass in gallium arsenide. This turning at ω_c is *cyclotron motion*, named for the machine that first used it to accelerate charges.

A motion that repeats at one frequency takes its energy in quanta, as a vibration of a spring does. Lev Landau found in 1930 that the energies of an electron turning in a magnetic field are $\hbar\omega_c(n + 1/2)$, with $n = 0, 1, 2$ and so on (Landau, 1930). Each such energy is a *Landau level*. The levels are far apart in a strong field: in gallium arsenide at 10 tesla, $\hbar\omega_c$ is 17 thousandths of an electron volt, the energy kT at 200 kelvin (computed), so at a few kelvin the levels stand sharply separate, with nothing between them. In a field this strong each electron's spin, pointing along or against the field, also splits each level in two, and each spin is counted below as a level of its own.

Each Landau level holds a great many states, one for each place in the sheet where an orbit can be centered, and the number is set by the flux. Each level holds exactly as many states as there are flux quanta of the single electron, h/e, passing through the sheet: eB/h states for each unit of area (Landau, 1930; standard quantum mechanics). The reason is the rule of Section II: an electron's states in the field are told apart by the phase they gather round the flux. Moving an orbit's center so as to take in one more flux quantum h/e turns its phase by one whole turn, which gives one new state. At 10 tesla, each level holds 2.4×10^{15} states in each square meter of sheet (computed). Here the unit is h/e and not the h/2e of Section III, because the charges in the sheet are single electrons, not pairs.

So the number of filled levels in a sheet is the number of electrons in each unit of area, n, divided by the number of states each level holds, eB/h. That ratio, $\nu = nh/(eB)$, read "nu", is the *filling factor*: the number of Landau levels the electrons fill. When ν is a whole number, the electrons fill exactly ν levels, and the next empty level lies a whole $\hbar\omega_c$ above the last filled one.

So we now know what states electrons take in a sheet in a strong field. They turn at the frequency eB/m, and their energies come in Landau levels $\hbar\omega_c(n + 1/2)$. Each level holds one state for each flux quantum h/e through the sheet, so a sheet of n electrons in each unit of area fills $\nu = nh/(eB)$ levels.

VI. The Quantum Hall Effect

In February 1980 Klaus von Klitzing, working at a high-field magnet laboratory in Grenoble, passed a current along the electron layer of a silicon transistor at 1.5 kelvin, in fields up to 18 tesla, and measured the voltage across the layer, the Hall voltage of Chapter 6, Section VII. The ratio of that voltage to the current, the *Hall resistance*, rose with the field in flat steps, not smoothly as the Hall effect in a metal does. On each step it took a value that did not depend on the sample's size, its shape or its number of electrons (von Klitzing, Dorda and Pepper, 1980). At the same fields the resistance along the current fell to zero. Why does a sheet of electrons in a strong field resist in steps?

When the electrons fill exactly ν Landau levels, a voltage along the sheet can give an electron only a small energy, far less than $\hbar\omega_c$, and every state within that small energy of an electron is already taken. So the voltage moves no electron into an empty state along its direction, and no current flows along the voltage, just as a full band carries no current (Chapter 6, Section V). The sheet does carry a current at right angles to the voltage. In crossed electric and magnetic fields every electron drifts sideways, whatever its state, at a speed equal to the electric field divided by the magnetic field (standard electromagnetism). The current across the voltage is then the number of electrons in each unit of area times their charge times that drift speed, in proportion to the voltage.

Two results follow. The resistance along the current is zero, since no voltage along the current is needed to carry it: the current runs at right angles to the voltage that drives it, and nothing is lost. And the Hall resist-

ance, the voltage across the sheet divided by the current along it, is B/(ne), the smooth Hall resistance that a metal shows (Chapter 6, Section VII), written for a sheet. With $n = \nu eB/h$ at exact filling, it is

$R_H = h/(\nu e^2)$,

read "R H", with ν a whole number. The unit h/e^2, the *von Klitzing constant* R_K, is 25,812.80745... ohms (computed from the exact h and e). On its plateaus the sheet's Hall resistance is R_K, $R_K/2$, $R_K/3$ and so on, and its inverse, the *Hall conductance*, is a whole number ν times e^2/h. The steps of the Hall resistance are the *quantum Hall effect*, and von Klitzing received the Nobel Prize in Physics for 1985 for finding the effect. Figure 10.1 draws its plateaus in outline.

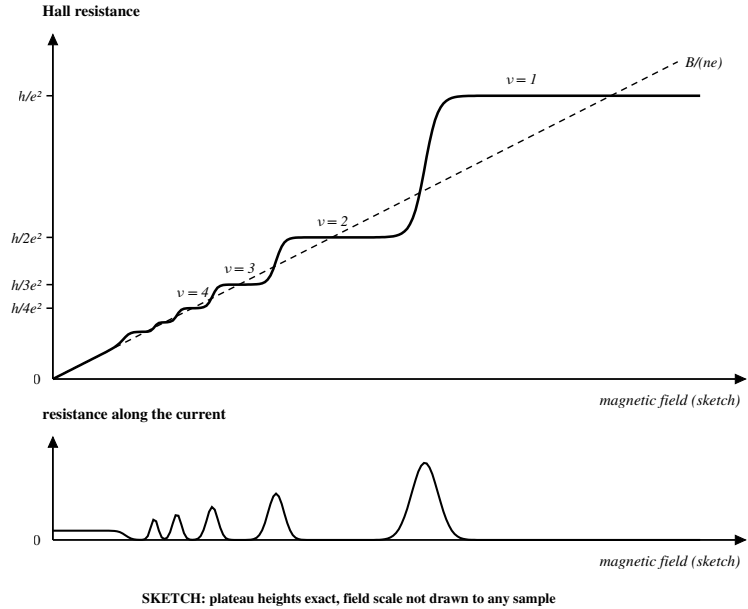


Figure 10.1. The quantum Hall plateaus in outline, drawn as a sketch. Upper panel: the Hall resistance of a sheet of electrons as the magnetic field rises. The dashed line is the smooth Hall resistance $B/(ne)$ of Chapter 6, and the plateaus lie at $h/(\nu e^2)$ for $\nu = 1$, 2, 3, 4 and higher, their heights drawn exactly, centered where the dashed line crosses them. Lower panel: the resistance along the current, zero on each plateau and rising between

plateaus, where the Fermi level passes through the states that reach across the sheet. The heights of the plateaus are exact; their widths and their places along the field show their form only.

The flaws of the sheet hold each plateau flat over a whole range of field, as Figure 10.1 shows, though the count so far gives the value only at exact filling, one field for each ν. A real sheet has impurities and rough boundaries. These turn some of each level's states into states held near one flaw, trapped in a small hollow or on a small hill of the electric energy, which reach across no distance and carry no current. Only the states near the middle of each level's energy reach across the whole sheet. As the field changes, the Fermi level, the energy of the top of the filled states (Chapter 2, Section XII), moves through those trapped states, filling or emptying them one by one. Meanwhile the states that reach across the sheet stay exactly as filled as before, so the current they carry, and with it the Hall resistance, does not change. Only when the Fermi level reaches the states that reach across, in the middle of the next level, does the Hall resistance move to the next plateau, and there the resistance along the current rises from zero (standard accounts of the quantum Hall effect). So the flaws that a careful maker removes from a transistor are what make the plateaus wide enough to measure on, and a perfectly clean sheet would show its whole numbers only at single fields.

So we now know why a sheet of electrons in a strong field resists in steps. Where the filled levels end in a gap, a voltage moves no electron along itself, so the resistance along the current is zero and the current flows across the voltage, in proportion to it. The Hall resistance then stands at $h/(\nu e^2)$, with ν the number of filled levels, and flaws that trap states between the levels hold it there over a range of field. The count used a clean sheet at exact filling, and so it raises a question: why do sheets full of flaws, of every shape and material, give the same steps to one part in ten billion?

VII. Why Each Plateau Is Exact: A Winding

A potter can work a lump of soft clay shaped like a ring into the shape of a cup with a handle, pressing and stretching it but never tearing it or joining two parts of it, and the ring's one hole becomes the hole of the handle. However the clay is pressed, the number of its holes stays one. To make it two or none, the clay must be torn or joined. A whole number that belongs to the shape as a whole cannot be changed by any smooth change of the shape. What whole number does a sheet of electrons carry in its Hall conductance?

Robert Laughlin answered in 1981 with an argument that uses only the rule of Section II and the gap (Laughlin, 1981). Bend the sheet into a ribbon whose ends meet, a short tube, and thread a magnetic flux through the tube along its axis, where no electron is. Then raise that flux slowly by one flux quantum h/e. In Box 10.2 we follow the electrons.

Box 10.2. The conductance as a winding

Premises. (1) Carried once round the tube, an electron's phase turns by $e\Phi/\hbar$, with Φ the flux threaded along the tube's axis (Section II); a flux of one quantum h/e turns it by exactly one whole turn. (2) A phase changed by a whole turn changes nothing that any measurement can find, so the electrons' states with the flux $\Phi + h/e$ are, as a set, the same as with the flux Φ (Section I, first and second results). (3) The Fermi level lies where the states that reach round the tube are all filled or all empty, with a gap of energy above the filled ones; trapped states, which reach no distance, are not moved by the threaded flux (Section VI). (4) A flux threaded through a loop and changed at the rate $d\Phi/dt$ makes a voltage round the loop of that size, $d\Phi/dt$, read "d phi d t" (Faraday's law of induction, standard electromagnetism). (5) A whole number cannot change under a smooth change (Section I, fifth result).

Steps. Raise the threaded flux slowly from Φ to $\Phi + h/e$. Slowly enough, with a gap above the filled states, no electron is lifted across the gap, so each filled state is carried smoothly into another filled state (3). At the end, by (2), the set of states is what it was at the start: the sheet is in its starting state, except that its filled states may have moved as a whole along the tube. The only way the electrons can have moved without changing the state of the sheet is for a whole number C of electrons to have been carried from one edge of the tube to the other. So in the time T taken to raise the flux by h/e, a charge Ce has crossed the sheet: a current Ce/T across the tube. By (4), the same change of flux has made a voltage $(h/e)/T$ round the tube, along the sheet. The current across, divided by the voltage along, is $Ce/T \div (h/e)/T = C\,e^2/h$. C is a whole number fixed by the filled states as a whole, so by (5) no smooth change of the sheet that keeps the gap open can change it: not a flaw, not an impurity, not a change of shape or size.

Result. The Hall conductance of a sheet whose filled states end in a gap is a whole number C times e^2/h, exactly. C counts how many electrons are carried from edge to edge as the flux grows by one quantum, a property of the filled states as a whole, and it is kept under every smooth change that keeps the gap.

In a crystal the same whole number has a form that can be computed from the bands. A state depends on settings, quantities that can be set from outside it, such as a field applied to it. Michael Berry showed in 1984 that a state carried slowly round a closed loop of its settings, and brought back to the same settings, returns with an extra turn of its phase, set by the loop alone (Berry, 1984). That turn is now called the *Berry phase*. For the electrons of a crystal the settings are the crystal momenta of the Brillouin zone. The zone closes on itself, since a crystal momentum carried across one edge of the zone comes back in at the opposite edge (Chapter 6, Section II). For a sheet the zone is two-dimensional and closes on itself in both directions, as the surface of a ring-shaped doughnut does. Cover the whole zone with small loops laid side by side, and add up the extra

turns of the filled states' phases round all of them. Each edge shared by two neighboring loops is gone round once in each direction, so its share cancels, and the sum is the turn round the outer edge of the whole patch of loops. The zone has no outer edge, since it closes on itself in both directions, so the phase must come back to itself, and the sum can only be a whole number of turns, as round any closed loop of Section I. That whole number of times the filled states' phases turn as the crystal momentum is carried over all its values is a *winding*, and for this case it is called the *Chern number*. David Thouless, Mahito Kohmoto, Peter Nightingale and Marcel den Nijs showed in 1982 that the Hall conductance of a sheet in a crystal is that Chern number times e^2/h, the same whole number as Laughlin's C (Thouless, Kohmoto, Nightingale and den Nijs, 1982). Thouless shared the Nobel Prize in Physics for 2016 for it. The Hall conductance is a winding.

The exactness follows. Flaws, impurities and the shape of the sheet change the states smoothly, so long as the gap stays open, and a smooth change cannot move a whole number. So the Hall conductance comes in exact whole multiples of e^2/h, the same in every sheet of every material. While the filled states end in a gap, the Hall conductance holds its whole number, and it can change only where the gap closes. The gap closes between the plateaus, where the Fermi level crosses the states that reach across the sheet and the resistance along the current rises from zero.

Measurements show what the winding requires. Sheets of gallium arsenide and of graphene, two materials with nothing in common but their electrons, give the same Hall resistance to within about one part in ten billion (Janssen et al., 2012). In graphene the plateaus have been seen at room temperature (Novoselov et al., 2007).

So we now know why each plateau is exact. Raising a threaded flux by one quantum returns the sheet to its own state while carrying a whole number of electrons from edge to edge, so the Hall conductance is that whole number times e^2/h. In a crystal the same number is the winding of

the filled states over the Brillouin zone, the Chern number. A whole number survives every smooth change that keeps the gap, so flaws, shapes and materials leave it exact.

VIII. Fractions

Passengers boarding an empty railway carriage, each wanting room, take one seat in every three, so that every passenger has an empty seat on each side. The carriage is a third full, and yet no one can move to another seat without coming closer to someone else. A crowd that keeps its members apart can settle into an arrangement fixed by the keeping apart alone. What do electrons that push one another hard do in a level only partly filled?

In 1982 Daniel Tsui, Horst Störmer and Arthur Gossard cooled a very clean sheet of electrons in gallium arsenide to below a kelvin, in a field so strong that the electrons filled only a third of the lowest Landau level (Tsui, Störmer and Gossard, 1982). They found a plateau there, with the Hall resistance at three times h/e^2 and the resistance along the current falling toward zero. By the count of Section VI, a third of a level has no gap of its own: two thirds of its states lie empty at the same energy. So the gap that the plateau needs comes from the electrons' push on one another, which in a partly filled level is the only energy left to arrange them.

Laughlin found the state in 1983 (Laughlin, 1983). His state gives, for every two electrons, a factor that falls to zero as the two approach, as the m-th power of their distance, with m a whole number, and it keeps every electron in the lowest level (Box 10.3). So the state keeps every electron away from every other, as the passengers keep their empty seats, and it fills exactly the fraction $1/m$ of the lowest level. It has a gap: compressing it or stretching it costs the push between the electrons, and its Hall resistance stands at m times h/e^2. Measurements show plateaus at exactly the fractions this state gives, 1/3 the first of them.

Which m are allowed is set by the electrons being fermions. Exchanging two electrons turns the factor for that pair into its negative raised to the power m, and so multiplies the state by -1 raised to the power m (Box 10.3). Exchanging two fermions of one kind must reverse the sign of their joint state (Section I, fourth result), so -1 raised to the power m must be -1, and m must be odd. So the simplest series of fractional states, for single electrons of one kind, has odd denominators: 1/3, 1/5, 1/7 of a level.

Box 10.3. Laughlin's state and its odd denominators

Premises. (1) Write each electron's place in the sheet as one complex number $z = x + iy$, read "z", with x and y its two coordinates and i a number whose square is -1; the size of $z_j - z_k$ is the distance between electrons j and k, and $z_k - z_j = -(z_j - z_k)$ (mathematics). (2) A state of N electrons in the lowest Landau level is a sum of products of powers of their z's, times a common factor that keeps them all in that level; a factor $z_j - z_k$ raised to the power m adds m to the highest power of each z, and the highest power of one electron's z sets how many of the level's states the electrons take up (Laughlin, 1983; standard quantum mechanics). (3) Exchanging two fermions of one kind reverses the sign of their joint state (Section I, fourth result).

Steps. Laughlin's state is the product, over every pair of electrons j and k, of $(z_j - z_k)^m$, times the common factor of (2), with m a whole number. By (1), each factor falls to zero as the m-th power of the distance between the two electrons as they approach. Each electron's z appears in $N - 1$ factors, so its highest power is $m(N - 1)$, and by (2) the N electrons take up about mN of the level's states: they fill the fraction 1/m of the level (Laughlin, 1983). Exchanging electrons j and k turns $z_j - z_k$ into its negative, by (1), so it multiplies $(z_j - z_k)^m$ by $(-1)^m$; the other factors are only reordered. By (3) the state must change sign, so $(-1)^m = -1$, and m is odd.

Result. Laughlin's state keeps every pair of electrons apart as the m-th power of their distance and fills 1/m of the lowest level, with m odd for single electrons of one kind: the fractions 1/3, 1/5, 1/7, with Hall resistances 3, 5 and 7 times h/e^2.

The charges that move in such a state are fractions of the electron's charge. Lifting the state by adding one flux quantum h/e at some point of the sheet, as Box 10.2 adds one round a tube, pushes away a share of the electrons' charge that is exactly 1/m of an electron's (Laughlin, 1983). That leaves a small region with that share missing. Such a region moves through the sheet as a body of its own, with charge e/m: in the 1/3 state, a third of the electron's charge. It is a collective excitation, a motion shared by many particles at once that comes in quanta (Chapter 5, Section IV). It is an arrangement of all the electrons of the sheet together, which exists only in the sheet, as the hole exists only in a band (Chapter 6, Section VII), and it is not a kind of particle. Its charge was measured in 1997, by the noise of the current that such charges carry, a current that comes in grains of e/3 and not of e (de-Picciotto et al., 1997; Saminadayar et al., 1997). Laughlin, Störmer and Tsui shared the Nobel Prize in Physics for 1998.

Many more fractions are found, and they follow a pattern. Jainendra Jain showed in 1989 that the electrons of a partly filled level, each bound to two quanta of the field's flux, act as new collective excitations, *composite fermions* (Jain, 1989). Composite fermions feel a smaller field, since the flux bound to them is taken from the field, and they fill whole Landau levels of their own. Filled p levels of composite fermions are the fractions p/(2p + 1) of the electrons' level: 1/3, 2/5, 3/7 and onward toward one half. These too have odd denominators. At exactly half a level, in one layer, the composite fermions feel no field at all, fill no levels, and make a metal of their own with no plateau (Halperin, Lee and Read, 1993).

An even denominator needs something that exchange does not reverse. In one layer of one kind of electron, the odd denominators come from the reversal of sign when two electrons are exchanged, so a state

with an even denominator must be built from something whose exchange does not reverse the sign. Pairs are the leading case: two fermions bound together make an even whole, which is not excluded, as Chapter 9, Section VII, showed for Cooper's pair. In 1987 Robert Willett and his colleagues found a plateau at a filling of 5/2, with two levels filled and the third half filled (Willett et al., 1987). The state that accounts for it is a state of paired composite fermions (Moore and Read, 1991). The collective excitations of that paired state carry a quarter of the electron's charge, as measured (Dolev et al., 2008), and they too are arrangements of the electrons of the sheet, not kinds of particle. Two layers give another route. Electrons in two sheets close together are told apart by their sheet, so exchange need reverse the sign only for two electrons of one sheet. So in a state of Laughlin's form for two sheets, the power for two electrons of one sheet must be odd, while the power for one electron in each sheet may be any whole number. With the power 3 within each sheet and 1 between the sheets, the state fills half a level counted over both sheets, an even denominator with no pairing (Halperin, 1983). It was found in 1992 in two sheets of gallium arsenide (Eisenstein et al., 1992; Suen et al., 1992).

So we now know what electrons that push hard do in a partly filled level. They take states that keep every electron apart, with a gap made by their push, so the Hall resistance stands on new plateaus at fractions of a level. For single electrons of one kind in one layer, exchange reverses the sign, so the simplest fractions have odd denominators. An even denominator needs something exchange does not reverse: pairs in one layer, or the two sheets of a double layer. The fractional charges that move in these states are collective excitations of the gathering of electrons.

IX. Crystals Whose Bands Wind

On the bridge between Macau, where cars drive on the left, and mainland China, where they drive on the right, the two lanes of traffic must cross over each other somewhere. No smooth bending of the road can carry a

left-hand lane into a right-hand one. Where the two rules meet, the road must have a crossing, and the crossing sits at the border because that is where the rule changes. In Section VII we found a whole number, a winding, carried by the filled states of a sheet as a whole. What happens at the border of a crystal whose filled bands carry such a number?

A sheet in a magnetic field winds because of the field, but the filled bands of a crystal can wind on their own, with no field from outside. Crystals of this sort make up *topological matter*: crystals whose filled bands carry a whole-number winding, or a two-valued index described below, that no smooth change keeping the gap can alter, and which therefore carry states at their boundaries. There are two kinds, and they differ in how they treat time reversal.

The first kind carries a whole-number winding, the Chern number of Section VII, and for this the crystal must break time reversal. Reversing time reverses every motion, so it turns a current flowing to one side of a voltage into a current flowing to the other side: it changes the sign of the Hall conductance. A crystal whose laws are unchanged by time reversal must therefore have a Hall conductance equal to its own negative, which is zero, and so a Chern number of zero. A nonzero winding needs time reversal broken: by a magnetic field from outside, as in the quantum Hall effect, or by magnets within the crystal itself. Duncan Haldane showed in 1988 that a crystal with no field from outside, but with a pattern of magnetic fields inside it that adds to nothing over each cell, can have a Chern number of one (Haldane, 1988). In 2013 Cui-Zu Chang and his colleagues found such a crystal, a thin film of bismuth antimony telluride with some chromium in it, whose magnetized chromium breaks time reversal (Chang et al., 2013). With no field applied, its Hall resistance stood at h/e^2. Such a crystal is a *Chern insulator*, also called a quantum anomalous Hall insulator, anomalous because its plateau needs no field from outside.

At the boundary of such a crystal the winding must change. Two crystals of different winding cannot be joined smoothly, since a winding cannot change smoothly, and empty space outside a crystal has the winding

zero. Where the winding changes, as where the two rules of the road meet, the gap must close, so the boundary carries states inside the crystal's gap. The crystal does not conduct within, and it does conduct along its boundary. No flaw that keeps the gap open can remove those states, since removing them would change the winding smoothly. In a sheet, whose boundary is a line, these are *edge states*; in a solid crystal, whose boundary is a surface, they are *surface states*. For a sheet with a winding of C, the edge carries C channels, and their electrons all move one way round the sheet, the way the field or the inner magnets turn them (Halperin, 1982). The current of the quantum Hall effect flows in the edge channels, and because the electrons of the channels all move one way, nothing turns the current back.

The second kind keeps time reversal, and its Chern number is zero; it is protected by time reversal itself. Its source is the rule of spin one half. Reversing time reverses an electron's spin, and reversing it twice turns the spin, in effect, through one full turn. A particle of spin one half returns to itself only after two full turns, so one full turn reverses its sign, as the belt with a buckle needs two turns to hang flat (Section I, eighth result). So reversing time twice reverses the state of an electron. Time reversal also turns every phase backward. So a state that time reversal carries into itself, turned by some fraction of a turn, is turned back by the same fraction when time is reversed a second time, and it returns with no reversal of sign. Every electron state does reverse its sign when time is reversed twice, so no electron state is its own partner under time reversal. Every state of energy E therefore has a partner of the same energy with opposite spin (Kramers, 1930). The rule that every state of energy E has a partner of the same energy with opposite spin is *Kramers' theorem*.

From Kramers' theorem a second *invariant* follows, an invariant being whatever stays the same under every change of setting (Volume One, Chapter 7, Section VI). Here the changes are every smooth change that keeps the gap open and time reversal unbroken, and this invariant exists only because time reversal holds. Count the boundary states inside the gap. They come in partners, one moving one way with its spin up, the oth-

er moving the opposite way with its spin down, since time reversal turns each into the other. A smooth change can push boundary states out of the gap only where two of them meet, and partners cannot meet each other, so a smooth change removes partner pairs only two at a time. So whether the number of such partner pairs crossing the gap is odd or even cannot change, and it is fixed by the filled bands as a whole. It is a two-valued index, a Z_2 *index* (read "Z two"), which can be only zero or one (Kane and Mele, 2005). When it is one, there is always at least one pair of boundary states crossing the gap, and nothing that keeps time reversal can remove it. A flaw that does not carry a magnet cannot turn an electron moving one way into its partner moving the other way, since the two are partners under time reversal, and so it cannot send the electron back. Time reversal is the whole of this protection: a magnetic flaw, which breaks time reversal, can open a gap in the boundary states. Crystals with the index one are the *topological insulators*, the crystals that keep time reversal and conduct on their boundaries.

What makes a crystal of this kind is spin-orbit coupling, the meeting of an electron's spin magnet with the magnetic field it finds, seen from the moving electron itself, from its motion through the electric field around it (Chapter 1, Section VI). Spin-orbit coupling is strong in heavy atoms (Volume One, Chapter 10, Section VI). In mercury telluride and in bismuth selenide it is strong enough to turn the order of the bands near the gap upside down, putting the band that would be the higher one below the other. A band order turned over in this way carries the index one, since the turning over brings one pair of partners across the gap (Bernevig, Hughes and Zhang, 2006).

In a sheet the boundary states run along the edges, one direction for each spin, and the sheet carries current along its edges with no field applied: the *quantum spin Hall effect*. Andrei Bernevig, Taylor Hughes and Shou-Cheng Zhang predicted it in thin layers of mercury telluride between layers of cadmium telluride (Bernevig, Hughes and Zhang, 2006). Markus König and his colleagues found it in 2007, in layers thick enough for the order of the bands to turn over, as predicted, and not in

thinner ones, where the order stays as it is (König et al., 2007). So the edge currents come with the turned-over bands, as the prediction says they must. In a solid crystal the boundary states cover the surface. In bismuth selenide the surface carries a single cone of states, whose energy rises in proportion to the momentum away from one point in every direction along the surface, with each electron's spin set at right angles to its motion (Xia et al., 2009; Zhang et al., 2009). The first solid crystal found with such surface states was bismuth antimony (Hsieh et al., 2008). The surface states are seen by *angle-resolved photoemission*, in which light knocks electrons out of the surface and the energies and directions with which they leave give the energy and momentum they had inside the crystal.

So we now know what happens at the border of a crystal whose bands wind. Where the winding or the two-valued index changes, the gap must close, so the boundary carries states inside the gap, on edges in a sheet and on surfaces in a solid. A whole-number winding needs time reversal broken and gives edge states that move one way only. A topological insulator, which keeps time reversal, carries the two-valued index, which exists because reversing time twice reverses an electron's state. Its boundary states come in partners of opposite spin moving opposite ways, which nothing that keeps time reversal can turn back.

X. What Is Fixed and What Is a Value

A recipe for a cake calls for two eggs. In every kitchen in the world the cake takes two eggs, though the eggs themselves weigh a little more in one kitchen and a little less in another. The two is a count, the same everywhere, and the weight of an egg is a value, measured. What in this chapter's results is a count, and what is a value?

Every result of this chapter has the same form: the Planck constant h and the electron's charge e, multiplied or divided by numbers that come from the structure. The flux through a ring is n h/2e; the frequency of a junction is 2eV/h, and its voltage steps nhf/2e; the Hall resistance of a

sheet is $h/(\nu e^2)$, with ν a whole number, or with the odd fractions of Section VIII. The Planck constant and the electron's charge are values; the factors by which they enter, the two of the pair and the whole numbers, are fixed by structure. So the ratios $2e/h$ and h/e^2 come out the same in every material. The two is fixed by the pair, an even whole of two electrons (Chapter 9, Section VII). The whole numbers are fixed by the one phase that must come back to itself round a loop (Section III), by the winding of the filled states (Section VII) and by the count of filled levels. The odd denominators of the simplest fractions are fixed by the reversal of sign when two electrons are exchanged (Section VIII), and the boundary states by the change of winding or index at a border (Section IX). No material can change any of these, since none of them is a value of the material: each is a count. The material's own values, its gap, its effective mass, its flaws, decide only where on the field the plateau stands and how wide it is, never its height. Chapter 9, Section XIII, showed the same split, a count fixed by structure beside values that differ from one material to the next, for the pair's charge, and in this chapter we carry it through every result.

Since 2019 the international system of units has been built on these counts. On 20 May 2019 the definitions of the units came to rest on fixed values of the constants of nature, among them the Planck constant, $h = 6.62607015 \times 10^{-34}$ joule seconds, and the electron's charge, $e = 1.602176634 \times 10^{-19}$ coulombs, both exact by definition (International Bureau of Weights and Measures, 2019). With h and e fixed, the Josephson constant $2e/h$ and the von Klitzing constant h/e^2 are exact too. So a laboratory makes the volt by a Josephson array and the ohm by a quantum Hall sheet, and each has the value the definition gives it. Before 2019, every laboratory used the same agreed values of the two constants, fixed in 1990, so that volts and ohms made in different countries matched one another, and those values agree with the exact ones of 2019 within the uncertainties stated for them (standard accounts of the Josephson voltage standard).

With the quantum Hall effect one can also measure the fine-structure constant, α, the strength of electromagnetism, $\alpha = e^2/(4\pi\varepsilon_0\hbar c) = 1/137.035999177$ (Chapter 1, Section VI). That value is uncertain by 21 in its last two digits, as CODATA 2022 gives it. Here ε_0 and its partner, the magnetic constant μ_0, are the constants of empty space, with $\varepsilon_0\mu_0 = 1/c^2$. The *impedance of empty space*, $Z_0 = \mu_0 c$, is the electric field of a light wave traveling through empty space divided by B/μ_0, its magnetic field B divided by the magnetic constant; it is measured in ohms, 376.730313412 ohms (CODATA 2022). Writing ε_0 as $1/(\mu_0 c^2)$ and $\hbar$ as $h/(2\pi)$, $\alpha = e^2\mu_0 c/(2h)$. So the von Klitzing constant set against the impedance of empty space is $R_K/Z_0 = h/(e^2\mu_0 c) = 1/(2\alpha)$, 68.517999588 (computed). *The Strengths of the Kinds*, Chapter 1, Section II, states this result, and with it that measuring the one against the other is a way of finding α. It also states that since 2019, with e, c and h fixed, μ_0 and ε_0 are no longer exact but measured through α, by $\mu_0 = 2\alpha h/(e^2 c)$. So a measurement of α, by the quantum Hall effect or another way, is now also a measurement of the magnetic constant. A sheet of electrons in a magnet thus reads a pure number of nature, the strength of electromagnetism, against a property of empty space.

So we now know how a material can measure a constant of nature to ten decimal places. The material does not supply the number. It supplies only counts, the two of the pair and the whole numbers of turns, windings and filled levels, which no flaw, shape or choice of material can change, and the values it multiplies them by are h and e alone. So the voltage of a junction for a given frequency, and the resistance of a sheet on its plateau, are the same in every sample to as many places as can be measured, and since 2019 they are exact.

In Use

Every voltmeter and every resistance meter that is calibrated traces its measure back, through a chain of comparisons, to the two effects of this chapter, the Josephson effect and the quantum Hall effect. In a national laboratory a Josephson array of some twenty thousand junctions is driven by microwaves near 75 billion swings each second, whose frequency is read from an atomic clock. It gives voltages up to ten volts that depend on nothing but that frequency and the exact ratio 2e/h. Arrays built so that their junctions can be switched in and out in groups give any voltage wanted, a group at a time (standard accounts of the Josephson voltage standard). Beside it a quantum Hall sheet, now often of graphene, which holds its plateaus at higher temperatures and lower fields than gallium arsenide, gives the ohm as $h/(2e^2)$ or another plateau. From the volt and the ohm come the ampere, by Ohm's law, and the watt. And the kilogram is now made in practice from the Planck constant by a balance that weighs a mass against an electric force read through these same two effects (International Bureau of Weights and Measures, 2019). A volt in one country is the same as a volt in another because a pair has two electrons and a phase comes back to itself.

The SQUID of Section IV reads the magnetic fields of the brain. The currents of thinking in the cortex make fields at the scalp of about ten millionths of a billionth of a tesla, ten femtoteslas, a femtotesla being 10^{-15} tesla (standard accounts of magnetoencephalography). Against them stand the Earth's field of some fifty millionths of a tesla and the magnetic noise of a city of about a ten-millionth of a tesla. David Cohen first read such fields in 1968 with a coil of copper wire, barely. In 1972, with one of the first SQUIDs in a room shielded from magnetic noise, he read them nearly as clearly as the electrodes of an electroencephalogram read the brain's voltages (Cohen, 1972). Today a helmet of about three hundred SQUIDs, cooled in liquid helium, maps where in the brain a burst of activ-

ity begins, millisecond by millisecond. Surgeons use it to find the source of an epileptic seizure and to map the regions of speech and movement that an operation must spare. *Magnetoencephalography*, the measuring of the brain's activity by its magnetic fields, rests on a ring that counts flux quanta and two junctions that read a fraction of one.

Summary

What I found in this chapter rests on three results: one phase that must come back to itself, a pair that carries two units of charge, and a winding that no smooth change can alter. From these, matter keeps numbers exactly. A charge's phase, carried round a loop, turns by its charge times the flux through the loop over ħ, the Aharonov-Bohm phase. The phase of a superconductor's pairs must come back to itself round a ring, so the flux through a ring is a whole number of flux quanta h/2e (Box 10.1): the factor two is the pair's, and the whole number is the ring's. Across a Josephson junction the pairs pass by the difference of two phases, so a current flows with no voltage up to the junction's critical current. A voltage V makes the difference advance at 2eV/ħ, so the current swings at the frequency 2eV/h, in a ratio that nothing but 2e and h enters and that is the same in every material. Microwaves turn back into voltage steps of hf/2e, and two junctions in a ring make the SQUID.

Electrons in a sheet in a strong field turn at eB/m in Landau levels, each with one state for each flux quantum h/e through the sheet. Where the filled levels end in a gap, no current flows along a voltage and the current flows across it, so the Hall resistance stands at $h/(\nu e^2)$, and flaws keep each plateau flat over a range of field. The plateaus are exact because the Hall conductance is a winding. Raising a threaded flux by one quantum carries a whole number of electrons from edge to edge (Box 10.2), the same whole number as the Chern number of the filled bands, and no flaw, shape or material that keeps the gap can change it. Electrons that push hard in a partly filled level take states that keep them apart,

Laughlin's states, at fractions of the level (Box 10.3). Exchange reverses the sign of two electrons' state, so for single electrons in one layer the simplest fractions have odd denominators. An even denominator needs something exchange does not reverse: pairs in one layer, as at 5/2, or the two sheets of a double layer. The fractional charges that move in these states are collective excitations of the gathering of electrons.

Crystals whose filled bands carry a winding or a two-valued index make up topological matter, and at their borders, where the number changes, the gap closes and edge or surface states conduct. A whole-number winding needs time reversal broken, in the quantum Hall effect and the Chern insulators, whose edge states move one way only. The topological insulators, mercury telluride and bismuth selenide among them, keep time reversal and carry the two-valued index. The index exists because reversing time twice reverses an electron's state, a particle of spin one half returning only after two full turns, so their boundary states come in partners of opposite spin moving opposite ways.

The Planck constant and the electron's charge are values; the factors by which they enter, the two in the pair's charge 2e and the whole numbers, are fixed by structure. So the ratios $2e/h$ and h/e^2 come out the same in every material, and since 2019 they are exact and set the volt and the ohm. Set against the impedance of empty space, the von Klitzing constant gives $1/(2\alpha)$, a way of finding the strength of electromagnetism. The values of each material determine only where along the field, and how widely, each of these whole numbers is seen.

Each of these numbers was read by passing a current through cold matter in a field, and the matter answered with an electric measure. Matter also answers light, and in a window and a mirror it answers very differently. Light passes through glass but not through metal. What does matter do to light?

✶

KEY CONCEPTS

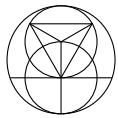
- **Aharonov-Bohm phase.** The turning of a charge's phase, carried round a loop, by its charge times the magnetic flux through the loop, divided by $\hbar$, even where the charge meets no field.
- **Josephson junction; DC and AC Josephson effects; Josephson constant.** Two superconductors joined through a layer that is not superconducting, about a nanometer thick; a steady (direct) current $I_c \sin \delta$ with no voltage, I_c being the junction's critical current; a current swinging back and forth (alternating) at $2eV/h$ under a voltage V; and the ratio $2e/h$, the same in every material.
- **Shapiro steps; SQUID.** Voltage steps of $hf/2e$ in a junction driven by microwaves of frequency f; a superconducting ring with two junctions whose largest current repeats once for each flux quantum, a magnetometer that reads fields of a few femtoteslas.
- **Two-dimensional electron gas; cyclotron motion; Landau level; filling factor.** A sheet of electrons free to move in two directions; their turning at eB/m in a magnetic field; the energies $\hbar\omega_c(n + 1/2)$, each with one state for each flux quantum h/e; and $\nu = nh/(eB)$, the number of levels filled.
- **Quantum Hall effect; Hall resistance; Hall conductance; von Klitzing constant.** The sheet's Hall resistance on flat plateaus at $h/(\nu e^2)$, with zero resistance along the current; the ratio of the voltage across the sheet to the current along it; its inverse; and $h/e^2 = 25{,}812.80745\ldots$ ohms.

- **Berry phase; winding; Chern number.** The extra turn of phase a state gathers when carried slowly round a closed loop of its settings; the whole number of times the filled states' phases turn as the crystal momentum is carried over all its values; and that number for a sheet or a crystal, equal to its Hall conductance in units of e^2/h.
- **Fractional quantum Hall effect; Laughlin state; composite fermions.** Plateaus at fractions of a level, made by the electrons' push; the state in which every pair of electrons is kept apart as the m-th power of their distance, m odd, filling $1/m$ of the level (Box 10.3); and electrons each bound to two flux quanta, filling whole levels of their own at the fractions $p/(2p + 1)$.
- **Collective excitation.** A motion shared by many particles at once that comes in quanta; the regions that carry the fractional charges $e/3$ and $e/4$ in the fractional states are collective excitations of the gathering of electrons, not kinds of particle.
- **Topological matter.** Crystals whose filled bands carry a whole-number winding or a two-valued index that no smooth change keeping the gap can alter, and which therefore carry states at their boundaries.
- **Chern insulator; edge states; surface states.** A crystal whose bands wind with time reversal broken by magnets within it, a quantum anomalous Hall insulator; boundary states in a sheet, along its edge; and in a solid crystal, over its surface.
- **Kramers' theorem; Z_2 index; topological insulator; quantum spin Hall effect.** Reversing time twice reverses an electron's state, so every state has a partner of the same energy and opposite spin; the two-valued index of a crystal that keeps time reversal; a crystal that keeps time reversal with that index equal to one, conducting on its boundary; and its two-dimensional form, with partners of opposite spin moving opposite ways along each edge.
- **Angle-resolved photoemission.** Light knocks electrons out of a surface, and the energies and directions with which they leave give the energy and momentum they had inside.

- **Impedance of empty space.** $Z_0 = \mu_0 c = 376.730313412$ ohms; set against it, the von Klitzing constant gives $R_K/Z_0 = 1/(2\alpha)$.
- **Magnetoencephalography.** The measuring of the brain's activity by its magnetic fields, with SQUIDs.

Part Four

Matter Seen Again



Chapter 11

Light in Matter

CHAPTER OVERVIEW

Light crosses glass with its crests advancing at two thirds of c, yet the speed of light is never changed. In this chapter we find how, and what follows. A passing light wave sets every bound electron of the glass swinging at the wave's frequency, nearly in step with the push below the electrons' natural frequencies. Each electron sends out a wave of its own, most strongly at right angles to its swing and not at all along it (the dipole pattern). The wave sent out by a thin sheet of such electrons is a quarter cycle behind the wave that drives them. So the sum of the entering wave and all those waves has its crests delayed: its phase advances at c/n, while every part of the sum travels at c (Box 11.1). Here n is the refractive index, the ratio of c to the speed at which the crests advance in the material. Near the natural frequencies the matter takes up light, which gives objects their colors. Above them the phase can advance faster than c, but the front of every change travels at c, and a charge moving faster than c/n trails a cone of Cherenkov light. At a surface the wave has one phase at each place, reached from either side, so the crests on the two sides must meet. So light bends where it enters glass, by a rule called Snell's law (Box 11.2, Figure 11.1). Part of the light is reflected, about four percent at glass, and from inside, beyond an angle called the critical angle, all of it is, which holds light in an optical fiber, a thread of glass that carries light. The lag depends on the frequency, so colors part. Air molecules are far smaller than the light they scatter, because the strength

of electromagnetism, α, is small, and they scatter as the fourth power of the frequency, so the sky lit from the side is blue and the low sun red. The electric field of light swings across its travel, and the direction of its swing is its polarization, of which light has two for each direction of travel, linear or circular as they are chosen. Crystals not alike in every direction slow the two linear ones differently, and at one angle, Brewster's angle, a surface reflects only one of them. Chiral molecules, those that differ from their mirror images, slow the two circular ones differently, so the plane of linearly polarized light, a sum of both, turns as it passes, and the mirror-image molecule turns it the other way. A metal's free electrons send light back below the plasma frequency, set by their number in each unit of volume, their charge and their mass, and let it pass above; copper and gold take their colors from their d bands. Through the electromagnetic field two beams pass through each other unchanged, since the photon carries no charge. Light acts on light through charges, in matter, where strong light makes new frequencies, and in empty space through pairs of charged particles that briefly appear and vanish, as measured at the Large Hadron Collider. And light acts on light through gravitation, since light shapes the geometry it follows. Photons are not excluded, so a passing photon raises the probability that an excited atom gives out a photon into its own state, in proportion to n + 1 by Einstein's balance of 1917 (Box 11.3). Where more atoms are ready to fall than to rise, which takes three or four levels, light grows as it passes, all in one state: the laser.

I. Slower, Yet Always at the Speed of Light

Chapter 10 ended with a question: light passes through glass but not through metal, so what does matter do to light?

Stand a pencil in a glass of water and look at it from the side: it seems broken at the surface, the part under water set off from the part above. Look down into a clear swimming pool and the bottom seems nearer than it is. Both come from one fact: light seems to cross water, glass and every

clear material more slowly than it crosses empty space, and its path bends where it enters them. That light crosses water more slowly than air was measured in 1850 (Foucault, 1850).

Yet the speed of light, c, is never changed. It is 299,792,458 meters each second, exact by the definition of the meter (Volume One, Chapter 7, Section III), and it is the same for every observer, however that observer moves. No body that has mass can be brought to it, since its energy grows without bound as its speed approaches c (Volume One, Chapter 10, Section II). Light is carried by the photon, the particle of light, which carries the electric force between charges, and electromagnetism is the force of electric charge, of light and of every chemical bond (Chapter 1, Section II). Nothing in the laws of electromagnetism gives light a slower speed inside matter: between the atoms of glass there is only empty space, and there light moves at c.

What is measured as slower is a property of a wave, and a few words about waves are needed. A light wave is an electric field and a magnetic field swinging back and forth at right angles to the wave's travel, each place of the wave reaching its greatest swing, a crest, in turn. Its *wavelength* is the distance from one crest to the next, and its *frequency* is the number of crests that pass a point in each second. Visible light has wavelengths from about 380 to 750 nanometers, its photons from 1.65 to 3.26 electron volts (Chapter 6, Section IX). The speed at which the crests move is the wave's *phase velocity*, the wavelength times the frequency. The crests mark the wave's phase, the stage of its swing at a place, counted as a fraction of a whole turn (Chapter 6, Section II). In empty space the phase velocity of light is c. In a material it is c/n, where n, the material's *refractive index*, is the ratio of c to the speed at which the phase of the wave in the material advances. For yellow light of wavelength 589 nanometers, n is 1.000293 for air at the freezing point and the pressure of the air at sea level, 1.333 for water, 1.458 for fused silica, between 1.50 and 1.54 for ordinary crown glass, and 2.417 for diamond (standard tables of refractive indices). In glass of index 1.5 the crests of light advance at two thirds of c, about 200,000 kilometers each second. The frequency is the same inside

the glass as outside, since every crest that enters must also leave. So the wavelength inside is shorter, by the factor n. The study of light and of what matter does to it is *optics*, and in this chapter we follow it from the slowing of light in glass to its multiplying in a laser.

So the reader's question is this: why is light slower in glass, when its speed never changes? We answer it in Section III, and from the answer we go on to the wider question of Chapter 10's ending, what matter does to light, which we take up in the later sections one effect at a time.

II. Charges Driven by a Passing Wave

A cork floating on a pond bobs up and down as a wave passes it, at the rhythm of the wave and not at any rhythm of its own. And as it bobs, it sends out small rings of its own across the water, at that same rhythm, which carry nothing into the pond but the wave's own beat. What does a light wave do to the charges in matter it passes through?

Every atom of glass holds electrons bound to it by the electric pull of its nucleus. The electric field of a passing light wave pushes on each of those electrons, back and forth, at the wave's frequency, and the electron, held to its atom as if by a spring, swings to and fro at that same frequency. Each bound electron has natural frequencies of its own, the frequencies at which its atom or molecule takes up light, set by its levels (Volume One, Chapter 7, Section VII). How it answers the push depends on where the light's frequency lies against them. Driven well below a natural frequency, the electron moves nearly in step with the push, a little way in the direction the field points. Driven well above, it cannot keep up, and it moves against the push; driven near it, it swings widely. Hendrik Lorentz described matter's answer to light in this way, each bound electron a charge on a spring, and the description is called the *Lorentz oscillator model* (standard optics). For the electrons of glass the natural frequencies lie in

the ultraviolet, since silica's gap is about 9 electron volts, far above every photon of visible light (Chapter 6, Section IX). So visible light drives them below their natural frequencies.

A charge that moves to and fro sends out light, as the charges running up and down a radio antenna do (Volume One, Chapter 7, Section I). So each driven electron sends out a light wave of its own, at the frequency that drives it. These waves are the *re-radiated* or *scattered* waves of the matter: light given off by charges that a passing wave sets swinging. An electron displaced from the center of its atom's positive charge makes, for that moment, a separation of charge. Its strength is the atom's *dipole moment*, the charge times the distance between the center of the positive charge and the center of the negative charge (Volume One, Chapter 11, Section IX), and a driven atom is a swinging dipole moment.

A swinging charge does not send its light out alike in every direction. A charge driven along one line sends out nothing along that line, and most at right angles to it (standard electromagnetism). The strength of what it sends out in a direction falls as the square of the sine of the angle between that direction and the line of the swing, the sine being 0 along the line and 1 at right angles to it (Chapter 10, Section IV, gave the sine). This uneven sharing of the re-radiated light among directions is the *dipole pattern*, and it determines, in Sections V, VII and VIII, which light a surface sends back and which light the sky sends down.

So we now know what a light wave does to the charges it passes. It sets every bound electron swinging at the wave's own frequency, nearly in step with the push when the frequency is below the electron's natural ones. Each swinging electron sends out a wave of its own at that frequency, most strongly at right angles to its swing and not at all along it.

III. The Sum of the Waves

A long column of soldiers marches across a field at a steady pace. At every row of the field a few soldiers fall in, each a pace behind the soldiers already marching, while as many at the head of the column leave it. Every soldier walks at the same speed throughout, yet the middle of the crowd falls back, row after row, against where it would have been, though no soldier ever slows. How can a sum of waves, each moving at c, fall behind?

Inside the glass, the field at any place is the sum of the wave that entered and every wave sent out by every driven electron between the entrance and that place. Each of those waves travels at c through the empty space between the atoms. Their sum is one wave of the same frequency, and the question is where its crests lie. In Box 11.1 we follow a thin sheet of the glass, as Richard Feynman did (Feynman, Leighton and Sands, 1963, Volume I, Chapter 31).

Box 11.1. Why the sum of the waves falls behind

Premises. (1) An electron of charge q_e and mass m, bound with the natural angular frequency ω_0, read "omega nought", and driven by an electric field $E_0 \cos \omega t$ of angular frequency ω, moves to and fro as $x = x_0 \cos \omega t$, with $x_0 = q_e E_0/(m(\omega_0^2 - \omega^2))$: in step with the field below ω_0, against it above (Section II; Feynman, Leighton and Sands, 1963, Volume I, Chapter 31). (2) A thin sheet of such electrons, N in each unit of volume and of thickness Δz, read "delta z", all swinging together, sends out on each side a wave whose field is $(N\Delta z\, q_e/(2\varepsilon_0 c))$ times their speed, pointing against their motion, and taken at the time the wave left the sheet (standard electromagnetism; Feynman, Leighton and Sands, 1963, Volume I, Chapters 30 and 31); here ε_0 is the electric constant, the number that sets, in the international units, how strong a field a given charge makes (Chapter 4, Section IX). The field is in proportion to the electrons' speed, not to their displacement, and the speed of a swing is greatest when the displacement is

zero: so the sheet's wave is a quarter cycle behind the field that drives it. (3) Adding a small wave a quarter cycle behind to a larger wave of the same frequency gives a wave delayed by a small part of a cycle, equal, in radians, to the ratio of the small wave's size to the large one's (mathematics: $\cos \omega t + \varepsilon \sin \omega t$ is nearly $\cos(\omega t - \varepsilon)$, for small ε, read "epsilon"). (4) A slab of thickness Δz and refractive index n delays a wave, against empty space, by the time $(n - 1)\Delta z/c$, which is the phase $\omega(n - 1)\Delta z/c$ (Section I, the definition of n).

Steps. By (1), each electron's speed swings with the size ωx_0. By (2), the sheet sends out a wave of size $(N\Delta z\, q_e/(2\varepsilon_0 c))\, \omega x_0$, a quarter cycle behind the wave that passes through it, and small when the sheet is thin. By (3), the passing wave and the sheet's wave together are the passing wave delayed by the phase $(N\Delta z\, q_e \omega x_0/(2\varepsilon_0 c))/E_0$, which with x_0 from (1) is $\omega N\Delta z\, q_e{}^2/(2\varepsilon_0 c\, m(\omega_0{}^2 - \omega^2))$. By (4), that delay is $\omega(n - 1)\Delta z/c$, so $n = 1 + Nq_e{}^2/(2\varepsilon_0 m(\omega_0{}^2 - \omega^2))$.

Result. Below the electrons' natural frequency, n is greater than one: the sum of the passing wave and the waves of the driven electrons has its crests delayed, sheet after sheet, so its phase advances more slowly than c. The delay grows as the frequency nears the natural one, so different colors are delayed by different amounts. Above the natural frequency, n is less than one, and the phase of the sum advances faster than c. Every part of the sum, the wave that entered and each wave sent out by a driven electron, travels at c; only the place of the sum's crests falls behind. For a thin gas this is the whole account; in a solid or a liquid each electron is driven also by the waves of its neighbors, and the same reasoning gives $n^2 = 1 + Nq_e{}^2/(\varepsilon_0 m(\omega_0{}^2 - \omega^2))$ with that correction made (Feynman, Leighton and Sands, 1964, Volume II, Chapter 32).

The account of the sum of the waves says more than Box 11.1 shows. Inside a thick slab, the waves sent out by all the electrons do two things at once. Layer by layer, the lagging waves of the electrons add up, and a little way inside the surface their sum holds two parts. One part is equal and opposite to the wave that entered, and it cancels that wave exactly. The

other part is a new wave that travels with the phase velocity c/n. Paul Ewald showed this for crystals in 1912 and Carl Wilhelm Oseen for any medium in 1915, and it is called the *Ewald-Oseen extinction theorem* (Ewald, 1912; Oseen, 1915). So the light that crosses a pane of glass is not the light that entered it. It is the sum of the light that entered and the light of every electron it set swinging, each part traveling at c, and the sum's crests advancing at c/n.

For a dense material the index can be traced to what each molecule does. A molecule's *polarizability* is how far its electrons are drawn for each unit of electric field (Volume One, Chapter 11, Section XIII). Counting the field of every neighbor that each molecule feels gives $(n^2 - 1)/(n^2 + 2) = N\alpha_p/(3\varepsilon_0)$, with N molecules in each unit of volume and α_p, read "alpha p", the polarizability of each: the *Clausius-Mossotti relation* (standard optics). It links the index of a liquid or a gas to the molecules it is made of, so the index of a substance can be computed from what is measured of its single molecules, and a denser form of one substance has the larger index.

So we now know why light is slower in glass, though its speed never changes. A light wave sets the electrons of the glass swinging, and each sends out a wave a quarter cycle behind the one that drives it. The sum of the entering wave and all those waves, each traveling at c, is a wave whose crests fall behind, so that its phase advances at c/n. The invariance of c stands: what is slower in glass is the place of the crests of a sum, and every wave that makes up the sum travels at c.

IV. Light Taken Up, and a Phase Faster than Light

In Volume One, Chapter 6, Section III, we pushed a child's swing in time with its own swing. Pushed at its own rhythm, the swing rises higher with every push and takes in all the effort given it, while pushed at another rhythm it barely moves. In Box 11.1 we found that an electron driven

near its natural frequency swings widely. What happens to light whose frequency matches the natural frequency of the electrons it drives, and what happens to light above it?

Driven near one of its natural frequencies, a bound electron swings widely and takes up the wave's energy, passing it on to the atom's other motions or lifting the atom to a higher level: the matter takes up the light, or *absorbs* it. The matter's taking up of the light is the absorption of Volume One, Chapter 7, Section VII, seen from the side of the wave. An atom takes up light at the frequencies of its levels, and a solid at the frequencies that can lift an electron across its gap (Chapter 6, Section IX). Light of a frequency the matter absorbs grows weaker as it goes, losing the same share of what is left in each equal thickness. So its strength falls as the exponential of the thickness: the *Beer-Lambert law*, after August Beer and Johann Lambert (standard optics). The taking up of light at some frequencies is why every object has the color it has. Its electrons take up some frequencies of the light that falls on it, by their levels, their gaps or their bands, and the eye sees what is sent back or passed, the light that is left. A leaf takes up red and blue light in its chlorophyll and sends back green; a ruby takes up green and violet in its chromium and passes red (Chapter 6, Section IX).

Above a natural frequency, in Box 11.1 we found n less than one: the phase of the sum advances faster than c. For X-rays, whose frequencies lie above those of the outer electrons of glass, the index of glass is less than one by a few parts in a million (standard optics). So for X-rays the glass is the side on which the phase advances faster, and X-rays meeting a glass surface from the air at a grazing angle are turned back entirely, as light is turned back inside glass beyond the critical angle of Section V. Yet a phase carries no signal. A wave that has gone on unchanged forever, with one frequency, crest after crest, tells nothing to anyone who receives it. To send a signal, the wave must be changed, started or stopped or shaped, and the change has a front, the first part of the wave to arrive. Ahead of the front nothing has yet reached the electrons, so nothing has set them swinging, and the front travels through the empty space between the atoms at c, in

every material, whatever its index (Sommerfeld, 1914; Brillouin, 1914). A pulse of light, the shape that carries a signal, moves at the speed of its envelope, the outline of its swings that rises and falls once over the pulse. That speed is the *group velocity*, which below the natural frequencies is less than c/n in ordinary glass, and no front of any change of light travels faster than c.

The front's speed has a second consequence. No electron answers a wave before the wave reaches it, so its answer at each moment is built only from the pushes it has already received. An answer built that way cannot slow the phase at some frequencies without taking up light at others, as a bell that rings only after it is struck has its pitch and its dying away tied together. So the way the index varies with frequency fixes how strongly the matter absorbs at every frequency, and the way it absorbs fixes the index. Ralph Kronig in 1926 and Hendrik Kramers in 1927 found the two formulas that tie them, the *Kramers-Kronig relations* (standard optics). A clear material slows visible light because it absorbs strongly elsewhere, in the ultraviolet and the infrared.

The phase velocity c/n below c has a companion that can be seen. A boat moving through water faster than the water's waves leaves a wake, a V of waves trailing behind it, because the waves it makes cannot keep up with it. A charged particle moving through glass or water faster than c/n, though still slower than c, does the same with light: the electrons it passes send out light that adds into a cone trailing behind it. That light is the *Cherenkov radiation*, found by Pavel Cherenkov in 1934 and explained by Ilya Frank and Igor Tamm in 1937 (Cherenkov, 1934; Frank and Tamm, 1937). The cone opens at the angle whose cosine is c/(nv), for a particle of speed v, the cosine being the number of Chapter 8, Section III, that tells how nearly two directions point the same way. In water, of index 1.333, an electron makes the cone once its speed passes three quarters of c, an energy of motion, a kinetic energy, of 0.26 million electron volts (computed). A particle moving at nearly c makes it at 41 degrees (computed). The blue glow of the water round the core of a pool reactor, a research reactor

whose core sits under deep water, is Cherenkov light. Great tanks of water lined with light detectors find neutrinos by the Cherenkov cones of the charged particles they strike (standard accounts of Cherenkov radiation).

So we now know what happens near and above the natural frequencies. Near them the matter takes up the light and turns colored or dark, the light's strength falling as the exponential of the thickness. Above them the phase can advance faster than c, but the phase carries no signal, and the front of every change travels at c. And because nothing answers before it is driven, the index and the absorption are tied together at every frequency.

V. Bending at a Surface

Waves rolling in from the open sea at a slant to a beach turn as they come near it, until their crests run nearly along the shore. The crests move more slowly in shallow water, so the end of each crest that reaches the shallows first falls behind the end still in deep water, and each crest, unbroken, wheels round. Light meets glass along a whole surface at once. Why does light bend where it enters glass?

At the surface between air and glass the field is one field. At each place of the surface the wave has one phase, whether it is reached from the air side or the glass side, since the field just above and just below a place of the surface is the field at that place (standard electromagnetism). So the crests of the wave in the air and the crests of the wave in the glass must meet the surface at the same places, crest to crest, all along it. The bending of light where it crosses from one material into another is *refraction*, and in Box 11.2 we find what the meeting of the crests requires of it. In the box we measure each direction by its angle from the *normal*, the line at right angles to the surface, and use the sine of that angle, which is 0 for light arriving straight on and grows to 1 for light grazing along the surface.

Box 11.2. Refraction from phase matching

Premises. (1) At each place of the surface between two materials the wave has one phase, reached from either side (standard electromagnetism). (2) The frequency is the same on both sides, so a wave whose wavelength is λ_0, read "lambda nought", in empty space has the wavelength λ_0/n_1 in the first material and λ_0/n_2 in the second (Section I). (3) A wave whose direction of travel makes the angle θ, read "theta", with the normal to the surface, the line at right angles to the surface, has its crests cross the surface with the spacing $\lambda/\sin\theta$, with λ its wavelength there (geometry).

Steps. By (1), the crests on the two sides meet the surface at the same places, so their spacings along the surface are equal: $(\lambda_0/n_1)/\sin\theta_1 = (\lambda_0/n_2)/\sin\theta_2$, by (2) and (3). So $n_1 \sin\theta_1 = n_2 \sin\theta_2$. From air, $n_1 = 1.00$, into glass, $n_2 = 1.50$, at $\theta_1 = 50$ degrees, $\sin\theta_2 = 0.766/1.50 = 0.511$, so $\theta_2 = 30.7$ degrees (Figure 11.1). Going the other way, from the material of higher index into the lower, $\sin\theta_2 = (n_1/n_2) \sin\theta_1$, which reaches one at the angle whose sine is n_2/n_1; beyond that angle no direction on the far side has crests spaced as widely as those arriving, so no wave can travel on the far side.

Result. Light crossing a surface bends so that $n_1 \sin\theta_1 = n_2 \sin\theta_2$, *Snell's law*: it bends toward the normal on the side where the phase advances more slowly. From the side of higher index, beyond the *critical angle*, whose sine is n_2/n_1, no wave can match the phase along the surface on the far side, and all the light is turned back: *total internal reflection*.

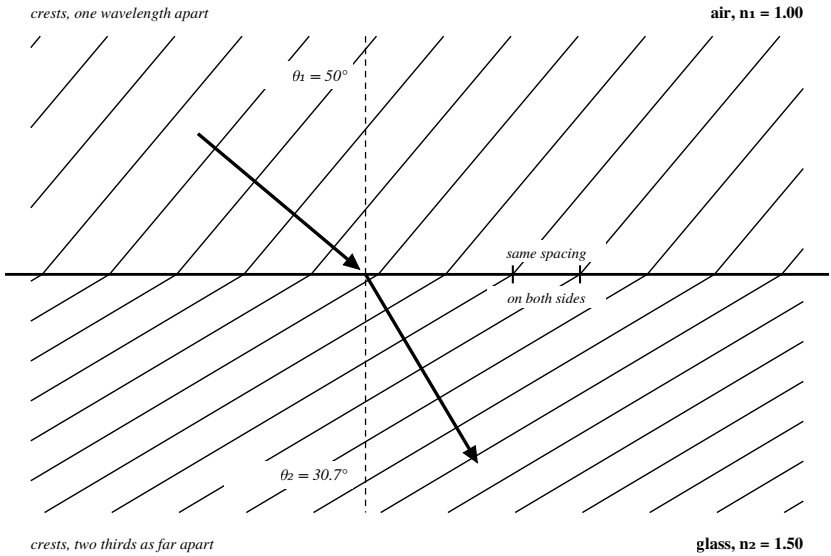


Figure 11.1. Refraction by phase matching at a surface, drawn from stated values: light from air (index 1.00) meets glass (index 1.50) at 50 degrees from the normal (the dashed line at right angles to the surface). The thin lines are the wave's crests, one wavelength apart in the air and two thirds as far apart in the glass, since the frequency is the same on both sides and the phase advances more slowly in the glass. The crests on the two sides meet the surface at the same places, with the same spacing along it, and that is possible only if the light in the glass travels at 30.7 degrees from the normal (the arrows), as Snell's law gives.

The bending is a matching of phase along the surface, and nothing in it needs the light itself to slow. The light that travels in the glass is the sum of Section III, whose crests advance at c/n, and the surface only requires that the crests of the sums on the two sides meet. Willebrord Snell found the law in 1621, in work he did not publish in his lifetime (Kwan, Dudley and Lantz, 2002), and the matching of crests gives it.

The phase of the wave also fixes the way that light takes. The ways of light are found where its phase is stationary: where a small change of the way leaves the phase, counted along the way, unchanged, apart from an amount far smaller than the change. The phase advances with time at the light's own rhythm, its frequency, so the phase counted along a way measures the time the light takes along it, and light's rays take the way of stationary time. The rule that light's rays take the way of stationary time is Fermat's principle of stationary time (standard optics).

Part of the light turns back. The electrons at and near the surface, driven by the wave, send out their waves in both directions, and those sent back toward the air add up to a *reflected* wave. It leaves the surface at the same angle at which the light arrived, since its crests too must match those arriving along the surface. How much is sent back was found by Augustin-Jean Fresnel in 1823 (Fresnel, 1823). For light meeting the surface straight on the share is $((n-1)/(n+1))^2$, the *Fresnel reflection*: 4.0 percent at glass of index 1.5, 2.0 percent at water and 17 percent at diamond (computed), which is part of why a cut diamond flashes. A window sends back about four percent of the light at each of its two faces, which is why at night, with the room lit, it shows the room.

Total internal reflection turns all the light back, with nothing lost. Inside glass of index 1.50 the critical angle is 41.8 degrees, in water 48.6 degrees, and in diamond 24.4 degrees (computed). So light that has entered a cut diamond meets most of its back faces beyond the critical angle and is turned back toward the viewer. Beyond the surface the field does not stop at once. It reaches into the air a fraction of a wavelength, falling as an exponential of the distance, the *evanescent wave*, and carrying no light away. Bring a second piece of glass within that distance, and light crosses the gap into it, as a particle tunnels through a barrier it could not cross (Chapter 3, Section III). Light crossing a narrow gap into a second piece of glass is *frustrated total internal reflection*. Some prisms use frustrated total internal reflection to split a beam in a chosen ratio by the width of the gap (standard optics). A thread of glass whose core has a slightly higher index

than the glass round it traps light in its core by total internal reflection at every bounce, and carries it round bends: an *optical fiber*, which the In Use section follows.

So we now know why light bends where it enters glass. At the surface the wave has one phase at each place, reached from either side, so the crests on the two sides must meet the surface at the same places. Since the crests are closer together in the glass, the light there must travel closer to the normal: $n_1 \sin \theta_1 = n_2 \sin \theta_2$. The surface's driven electrons also send part of the light back, about four percent at glass. And from inside, beyond the critical angle, no wave on the far side can match the phase, so all the light turns back.

VI. Colors Part

In 1666 Isaac Newton let a narrow beam of sunlight through a hole in his shutter and through a glass prism, and on the far wall it fanned out into a band of colors, red at one end, violet at the other. Gathered together again, the colors made white light once more (Newton, 1672). White light is a mixture of colors, and glass bends each by a different amount. Why does glass bend violet light more than red?

In Box 11.1 we found that the lag of the sum grows as the light's frequency nears the electrons' natural frequency. The natural frequencies of glass lie in the ultraviolet, beyond violet light, so violet light, of the highest visible frequency, is nearest them. The electrons answer it more strongly, the sum's crests fall further behind, and the index is larger. Different colors are slowed differently, so by Snell's law they bend differently, and a mixture of colors parts into its colors. That parting is *dispersion*, the change of the refractive index with the frequency of the light. For a common crown glass, the index is 1.5224 for blue light of 486 nanometers, 1.5168 for yellow light of 588 nanometers and 1.5143 for red light of 656 nanometers (computed from the glass maker's formula, the Sellmeier for-

mula with the coefficients for that glass). A prism of it with faces at 60 degrees turns the blue light about 0.7 degrees more than the red (computed).

The forms in which the index is written follow from Box 11.1. Augustin-Louis Cauchy wrote it in 1836 as a constant plus a term falling as one over the square of the wavelength, which is Box 11.1's formula far below a natural frequency (standard optics). Wolfgang Sellmeier wrote it in 1872 as a sum of terms, one for each natural frequency, each of Box 11.1's form, which fits the index of a glass over its whole clear range with three such terms (Sellmeier, 1872). A rainbow is dispersion in drops of rain: sunlight bends into each drop, reflects from its back and bends out again. Since each color bends by its own amount, each leaves at its own angle, red at about 42 degrees from the point opposite the sun and violet at about 40 degrees (standard accounts of the rainbow).

So we now know why colors part in glass. The lag of the sum depends on how near the light's frequency is to the natural frequencies of the electrons. So the index is larger for violet light, nearer the ultraviolet, than for red, and each color bends by its own amount.

VII. Why the Sky Is Blue

On a clear day the sky is blue overhead, and paler near the horizon, where sky and ground seem to meet. At sunset the sun is red, and the sky round it orange and red. In space, above the air, the sky is black, and the sun is white. The light of the sky is sunlight sent toward us sideways by the air. Why is it blue, and why is the setting sun red?

A molecule of air is far smaller than the wavelength of visible light, so the light's field is the same across the whole molecule at each instant, and the molecule answers as one driven charge. How much smaller follows from the atom. A molecule is about as large as its atoms, a few tenths of a nanometer, and an atom's size is the Bohr radius, a_0, read "a nought", 0.0529 nanometers (Volume One, Chapter 7, Box 7.1). The light that an

atom takes up and sends out matches the energies of its levels, which are about the binding of one electron round a charge held fixed, the Rydberg energy, $\alpha^2 m_e c^2/2$ (Chapter 1, Section VI). Here m_e is the electron's mass and α the fine-structure constant, the strength of electromagnetism, 1/137.035999177 (Chapter 1, Section VI). A photon of that energy has the wavelength hc divided by it, which is $4\pi a_0/\alpha$: 91.1 nanometers, longer than the atom by the factor $4\pi/\alpha$, about 1,700 (computed). So the light that atoms take up and send out is about two thousand times their size, and visible light, of lower energy, is longer still. Light of 500 nanometers is about 9,400 times the Bohr radius and nearly two thousand times the size of a molecule of air. Because α is small, molecules are always far smaller than the light that drives them.

A charge much smaller than the wave sends out light in the dipole pattern of Section II, with a power that rises as the fourth power of the frequency. The field that a single small charge sends out, at a distance, is in proportion to how fast its swing speeds up and slows down, which for a swing of fixed size grows as the square of the frequency, and the power goes as the square of that field (standard electromagnetism). A whole flat sheet of charges swinging together, as in Box 11.1, is different: the fields of all its charges add, and their sum follows the charges' speed, which is why we speak of speed in the box. Lord Rayleigh found this law of scattering by small particles in 1871 (Rayleigh, 1871), and it is called *Rayleigh scattering*. Blue light of 450 nanometers is therefore scattered by the air about 5.9 times as strongly as red light of 700 nanometers (computed). The rest of the account of the sky's color is what is observed: the sun lights the air from one side with a mixture of all visible colors. Looking at the sky away from the sun, the eye sees only light that the air has sent sideways, and that light is rich in the short wavelengths: the sky is blue. Looking at the sun when it is low, through a long path of air, the eye sees the light that is left after much of the short wavelengths has been sent aside: the setting sun is red.

Blue rather than violet fills the sky, though violet light is scattered more strongly still, for three reasons together. Sunlight holds less violet than blue: the sun's surface, at about 5,772 kelvin, sends out most strongly near 500 nanometers by Wien's law (Chapter 2, Section XIII), and less and less toward the violet (computed). The eye is far less sensitive to violet than to blue. And the light of the sky is not one color but a mixture of all the colors, weighted toward the short wavelengths, which the eye sees as a pale blue (standard accounts of the color of the sky).

The dipole pattern also sets the polarization of the sky's light, which Section VIII defines. Sunlight drives each molecule's electrons across the line from the sun, in every direction across it. Seen from a direction at right angles to the sunlight, the swings along the line of sight send nothing toward the viewer, since a charge sends nothing along its line of swing. Only the swings across both the sunlight and the line of sight send light there. So the light of the sky at 90 degrees from the sun swings mostly in one direction: it is polarized, as a polarizing filter turned against that part of the sky shows, darkening it (standard accounts of the polarization of skylight).

Particles that are not small against the wavelength scatter differently. The droplets of a cloud, some micrometers across, are many wavelengths of light wide, and they scatter every color about equally, in a way first worked out by Gustav Mie in 1908, *Mie scattering* (Mie, 1908). So clouds are white or, thick enough, gray. Between molecules and cloud droplets lie the particles of smoke, fog and colloids, whose scattering makes a beam of light visible from the side, as a sunbeam in a dusty room or a headlight's beam in fog is. The scattering that makes a beam of light visible from the side is the *Tyndall effect*, after John Tyndall, who studied the effect in 1869 (standard optics). A small share of the light scattered by molecules comes out with its frequency changed, raised or lowered by a frequency at which the molecule vibrates, because the molecule takes energy from the light into its vibration or gives energy to it. The change of frequency in scattered light is the *Raman effect*, found by Chandrasekhara Venkata Ra-

man and Kariamanikkam Srinivasa Krishnan in 1928 (Raman and Krishnan, 1928). Chemists identify molecules by the Raman effect, from the light the molecules scatter.

So we now know why the sky is blue. Air molecules are far smaller than the wavelength of light, because α is small, so each answers as one driven charge and scatters with a power rising as the fourth power of the frequency. Sunlight, a mixture of colors, lights the air from the side, so the sky sends us its blue and the low sun, seen through much air, is left red. And the dipole pattern makes the sky's light polarized at right angles to the sun.

VIII. Two Polarizations

Tie a long rope to a post and shake its free end up and down, and a wave runs along it swinging up and down. Shake it side to side, and the wave swings side to side. Pass the rope through a picket fence with upright slats, and the up-and-down wave passes through the gaps while the side-to-side wave is stopped. A wave that swings across its direction of travel can swing in more than one way. In how many ways can light swing, and what does matter do to each?

The electric field of light swings at right angles to the light's travel, and the direction of its swing is the light's *polarization*. For light traveling in one direction there are exactly two independent polarizations: every way the field can swing across the travel is a sum of two chosen ones (standard electromagnetism). The two can be chosen in more than one way, and I use two choices. In the *linear* choice the field swings along one line, for instance up and down, or side to side. In the *circular* choice the field keeps its size and turns round as the wave passes, clockwise or counterclockwise as seen by the light's receiver. Each linear polarization is the sum of the two circular ones in equal shares, and each circular polarization is the sum of the two linear ones, a quarter cycle apart. Sections VII and VIII use the linear choice, and Section IX the circular one.

Why two, and not three? A carrier with mass has a third way of turning, along its line of motion, as we found in Chapter 8, Section VIII, for the W and the Z. A particle of spin one is found along any chosen axis in one of three ways, its angular momentum along that axis being $-\hbar$, 0 or $+\hbar$ (Chapter 1, Box 1.3), and a change of the chosen axis carries each of the three into a mixture of all three (standard quantum mechanics). A carrier with mass can be taken where it is at rest, and there every axis is open to it, so all three ways are carried into one another. Light has no such place: it moves at c for every observer (Section I), and in the zoo's words, "Having no rest mass, it has no rest to depart from: it is never at rest" (The Story of the Particles, Level 0, Section II). So the only turns that leave light's motion as it was are the turns about its own line of travel, and such a turn carries each of the two circular polarizations into itself, never into a third way of turning. Nothing in light's motion, then, joins a third way of turning to its two, and its field swings only across its travel, in the two polarizations above (Wigner, 1939). A carrier with mass, which can be at rest, does carry the third, and the W and the Z take theirs from the Higgs field. Physicists call that third way of turning longitudinal, along the line of motion, and The Branches of the Kinds states it so: "Three Goldstone bosons become the longitudinal $W^{\pm}$ and Z^0, giving them mass" (Chapter 4, Box 4.3), a Goldstone boson being the quantum of Chapter 8, Section VI.

In glass, water or air, a material alike in every direction, the two polarizations meet the same answer from the electrons and are slowed alike, so the index is the same for both. In a crystal that is not alike in every direction, the electrons are held more stiffly along some directions than along others. So light whose field swings along one direction of the crystal meets a different answer from light whose field swings along another, and the two linear polarizations are slowed differently: the crystal has two indices. A beam entering it at a slant is bent by two amounts and splits in two, and print seen through such a crystal is seen twice. The splitting of a beam in two is *birefringence*, double refraction. Rasmus Bartholin found bi-

refringence in 1669 in calcite, a clear crystal of calcium carbonate. The two indices of calcite are 1.658 and 1.486 for light of 590 nanometers (standard tables of birefringence).

At one angle of a surface only one polarization is sent back, and the dipole pattern gives the reason. The reflected light is sent out by the electrons just inside the surface, driven by the light in the glass. The arriving light, the reflected light, the light in the glass and the normal all lie in one plane, the *plane of incidence*. When the light in the glass travels at right angles to the direction the reflected light would take, the electrons driven by the polarization that lies in the plane of incidence swing exactly along the reflected direction, and a charge sends nothing along its line of swing. So for that polarization nothing is reflected. Only the polarization at right angles to the plane of incidence, whose electrons swing across the reflected direction, is sent back. The angle of incidence is the angle at which the light arrives, measured from the normal, and the tangent of an angle is its sine divided by its cosine. By Snell's law the direction in the glass and the reflected direction are at right angles when the tangent of the angle of incidence equals n_2/n_1: $\tan \theta_B = n_2/n_1$, read "tan theta B", which is 56.3 degrees for glass of index 1.5 and 53.1 degrees for water (computed). That angle is *Brewster's angle*, found by David Brewster in 1815 (standard accounts of Brewster's angle). Light reflected from a lake or a wet road near that angle swings mostly side to side, which is why glare from water is mostly of one polarization.

A *polarizer* passes one linear polarization and stops the other, as the picket fence does. The common sheet polarizer holds long molecules lined up in one direction, whose electrons can swing along them and take up the light that drives them that way, so that only light swinging across them passes (standard optics). A thin plate of a birefringent crystal, cut so that one polarization falls a quarter cycle behind the other in crossing it, turns linear polarization into circular: a *wave plate*. It does so because a circular polarization is the sum of two linear ones a quarter cycle apart. A *liquid-crystal display* works by both. Each small region holds a liquid crystal,

a liquid whose rod-like molecules share a direction (Chapter 4, Section VIII), between two polarizers set at right angles. The twisted arrangement of its molecules turns the light's polarization so that it passes the second polarizer, and a voltage that lines the molecules up stops the turning, so the region goes dark (standard accounts of liquid-crystal displays).

So we now know what matter does to light's two polarizations. A material alike in every direction slows both alike. A crystal that is not slows the two linear polarizations differently and splits a beam in two. And at Brewster's angle the driven electrons send nothing along their line of swing, so only one polarization is reflected.

IX. Mirror-Image Molecules Seen in Light

A left glove does not fit a right hand, though it is the right glove's mirror image, with every finger the same. No turning of the left glove makes it a right one. A spiral staircase winds either clockwise or counterclockwise as it rises, and so does the thread of a screw. Many molecules are like that too: a molecule that is not the same as its mirror image, as a left hand is not the same as a right, is *chiral*, from the Greek for hand. Sugar is chiral, and so are all the amino acids of living things but the simplest, glycine. Can light tell a molecule from its mirror image?

Light can tell a molecule from its mirror image, through the circular polarizations of Section VIII. A chiral molecule or crystal is wound one way, and its electrons, driven along the winding, answer a field turning clockwise differently from a field turning counterclockwise. So the two circular polarizations are slowed differently, and the material has a slightly different index for each. Linearly polarized light is the sum of the two circular polarizations in equal shares. Crossing the material, one of the two falls behind the other, and their sum is still linear, but along a line that has turned. So the plane of linearly polarized light turns as the light passes through a chiral material, by an angle that grows with the thickness: *optical activity*. The mirror-image material, wound the other way,

turns the plane by the same angle in the other direction. François Arago found the turning in quartz in 1811 and Jean-Baptiste Biot in sugar solutions and other liquids from 1815 (standard accounts of optical rotation). Louis Pasteur found in 1848 that the crystals of one salt of tartaric acid come in two mirror-image forms, which, sorted by hand and dissolved, turn the plane in opposite directions (Pasteur, 1848). So the chirality of matter, the difference between a molecule and its mirror image, which a mirror exchanges, shows in light.

Chiral matter can also take up the two circular polarizations differently: *circular dichroism*. By the Kramers-Kronig relations of Section IV the turning and the unequal taking up come from the same answer of the same electrons, so chemists measure either to learn the winding of large molecules such as proteins (standard optics). The sugar industry measures the concentration of a syrup by how far it turns the plane of polarized light (standard accounts of optical rotation).

A magnetic field can turn the plane of polarization too, in any material, chiral or not: Michael Faraday found in 1845 that glass in a magnetic field along the light's path turns its plane, the *Faraday rotation* (standard optics). The two turnings are told apart by sending the light back. In a chiral liquid, light sent through and reflected back has its turning undone, since the winding of the molecules looks the same from either end. In a magnetic field the turning is doubled, since the field's direction does not reverse with the light's.

So we now know that light can tell a molecule from its mirror image. A chiral material slows the two circular polarizations differently, so the plane of linearly polarized light, which is a sum of both, turns as it passes, and the mirror-image material turns it the other way.

X. Metals Shine, Then Turn Clear

A spoon of polished silver sends back almost all the light that falls on it, and so does the thin layer of aluminum behind the glass of a mirror. Yet Robert Wood found in 1933 that a thin film of sodium, which sends back visible light as any metal does, lets ultraviolet light of wavelengths shorter than about 210 nanometers through as glass lets visible light through (Wood, 1933; Chapter 6, Section IX). Why does a metal shine, and why does it turn clear at short enough wavelengths?

The free electrons of a metal are held by no spring: they belong to the whole piece of metal, and nothing pulls each back to an atom (Chapter 6, Section V). In Box 11.1 that is the case of a natural frequency of zero. For a metal's dense crowd of free electrons the dense form of the result gives $n^2 = 1 - {\omega_p}^2/\omega^2$, where ${\omega_p}^2 = Ne^2/(\varepsilon_0 m_e)$, with N the number of free electrons in each unit of volume, as in Box 11.1, and n the index. That ω_p is the plasma frequency of Chapter 4, Section IX, the frequency at which the free electrons swing together through the ions, set by the number of free electrons in each unit of volume, their charge and their mass, and by nothing else.

Below the plasma frequency, n^2 is negative. No ordinary number has a negative square, so no index of the ordinary kind fits, and no wave travels into the metal: the field, instead of swinging forward, falls off with depth. The free electrons swing all together, against the push, so strongly that the waves they send out cancel the entering wave within a short depth and send the light back. The field reaches into the metal only that short depth, falling as an exponential, its *skin depth*, about c/ω_p: 18 nanometers for copper and 33 for sodium (computed from their densities of free electrons). So a metal sends back all light below its plasma frequency, and that is its shine. Above the plasma frequency, n^2 is positive, though less than one, so a wave travels. The light changes direction too fast for the free electrons to follow, and it passes, and the metal is clear. For sodium the

plasma frequency corresponds to a wavelength of 210 nanometers, which is Wood's edge, and for copper to 115 nanometers, far in the ultraviolet (computed; Chapter 6, Section IX). The same reasoning, with free electrons far fewer, gives the plasma frequency of the upper atmosphere, nine million swings each second, below which radio waves are sent back to the ground (Chapter 4, Section IX).

All metals shine below their plasma frequency, but not all are the color of silver. The colors of copper and gold come from a second source: their filled d bands lie only about 2 electron volts below their Fermi levels (Chapter 6, Section IX). Light of enough energy to lift an electron from a d band into the empty states above is taken up, green, blue and violet light among it, so copper looks reddish and gold yellow. Silver, whose d band lies near 4 electron volts down, sends back every visible color alike. For gold the gap is about 2.4 electron volts, narrowed by relativity, the account of motion near the speed of light, which the fast inner motion of gold's electrons needs (Volume One, Chapter 10, Section VIII). The plasma edge of these metals lies in the ultraviolet, and their colors are set by the bands.

So we now know why a metal shines and when it turns clear. Its free electrons, held by no spring, swing together against light below their plasma frequency, which is set by their number in each unit of volume, their charge and their mass. They send that light back within a few tens of nanometers, and above the plasma frequency they cannot follow, and the light passes. Copper and gold take their colors from their d bands.

XI. Light Passing Through Light

Two flashlights shone across a dark room cross each other's beams, and each beam goes on as if the other were not there: neither bends, dims or changes color where they cross. Two people talking across a room hear each other through a third conversation crossing between them. Does light act on light? The question belongs to this chapter's, what matter does

to light, because the only ways light can act on light are through matter, through the charges that matter is made of, and through the geometry that matter and light both shape.

Through the electromagnetic field alone, two beams of light pass through each other unchanged. The photon carries no electric charge, so the electromagnetic field does not act on itself, and its laws are *linear*: any two waves the laws allow, added, make a third wave the laws allow, each going on as it would alone (standard electromagnetism). In Volume One, Chapter 7, Section II, we found for the same reason, that the photon carries no charge, that the field of a charge does not act on itself. So in empty space, through the field alone, two beams pass through one another and neither changes.

Light acts on light through charges. In matter, the electrons that two beams drive together answer, when the beams are strong, with waves that neither beam would make alone, which we find in Section XII. In empty space the field's ground state holds pairs of charged particles that briefly appear and vanish (Volume One, Chapter 8, Section VI). The uncertainty principle of energy and time, the conjugate pair of Chapter 1, Section II, allows each pair for a time about $\hbar$ divided by the energy of its mass. Two photons can act on each other through such pairs. Every kind of charged particle takes part, each through pairs of itself and its antiparticle, and at the energies of ordinary light the electron, the lightest charged particle, takes the largest part. Hans Euler and Werner Heisenberg computed the effect in 1936 (Euler and Heisenberg, 1936), and it is so slight that no lamp or laser makes it large enough to see. It has been seen with the strongest fields there are. When two nuclei of lead pass close by each other at nearly the speed of light in the Large Hadron Collider, the fields round them act as dense clouds of photons, and pairs of photons from the two clouds scatter off each other. The ATLAS collaboration saw this scattering of light by light, first in 2017 and with certainty in 2019 (ATLAS Collaboration, 2017; ATLAS Collaboration, 2019).

Light acts on light through gravitation too. Light follows the geometry of space and time and bends where that geometry is curved. *The Gravitational Passage*, Chapter 16, Section III, names "the deflection of light", the bending of starlight by the sun, among the well-known features of the field of gravitation outside a mass, which its equations give. And light shapes the geometry, since it carries energy and momentum. *The Gravitational Passage*, Chapter 12, Section V, states it: "The right-hand side of the Einstein equations contains the stress-energy tensor $T_{\mu\nu}$, which encodes the energy, momentum, and stress of the matter and radiation fields". The Einstein equations are the equations of gravitation: on one side the curving of space and time, and on the other, the right-hand side, what fills space and time. The *stress-energy tensor* is the quantity that gives, at each place, the density and the flow of energy and momentum. Its symbol $T_{\mu\nu}$, read "T mu nu", carries two small letters because it has a value for each pair of directions in space and time. The radiation it names is light. So each of two beams curves the geometry where it passes, and the other bends where the first has curved it: two beams act on each other through gravitation. Richard Tolman, Paul Ehrenfest and Boris Podolsky worked out in 1931 how (Tolman, Ehrenfest and Podolsky, 1931). Beams moving in opposite directions attract each other, and beams moving side by side in the same direction do not. For beams moving together the pull of the one beam's energy is canceled by the effect of its motion, as two charges moving side by side near the speed of light have their electric push canceled by their magnetic pull. The pull is far too weak ever to be seen: a beam of a thousand watts carries, in each meter of its length, the energy of a mass of about 4×10^{-23} kilograms (computed), far less than any mass whose pull on another has been measured.

So we now know whether light acts on light. Through the electromagnetic field alone, two beams pass through each other unchanged, because the photon carries no charge and the field is linear. They act on each other through charges, in matter, and in empty space through pairs of charged

particles that briefly appear and vanish, seen at the Large Hadron Collider. And they act on each other through gravitation, because light shapes the geometry it follows.

XII. New Colors from Strong Light

A loudspeaker played gently gives back the music as it was recorded. Turned up past what its cone can follow, it buzzes, and the buzz holds tones that were never in the music, at twice and three times the frequencies that were. What does matter do to light that drives it hard?

In Box 11.1 we took each electron's answer to be in proportion to the push, as a spring's stretch is in proportion to the weight hung on it. That holds for gentle light. When the driving is strong, the hold on the electron is not exactly in proportion to its displacement: an electron pushed far from its place feels a pull that is no longer a fixed multiple of the distance. Its swing is then not a pure swing at the driving frequency, and it sends out light at frequencies that were not driven. Light sent out by matter at frequencies that the light driving the matter did not have is *nonlinear optics*.

Which new frequencies appear depends on the symmetry of the hold. Where the hold is the same on both sides of the electron's place, as it is in any material whose arrangement looks the same reversed through a point, the answer reverses exactly when the push reverses. So it holds only odd powers of the push: three times the driving frequency, and sums of three frequencies, appear, and nothing at twice. Every material can do this, glass and water included, and the index itself then changes with the light's strength, the *Kerr effect* (standard optics). Where the hold is not the same on both sides, in a crystal with no center of symmetry, such as quartz, the answer to a push one way differs from the answer to a push the other way. There even powers appear too: twice the driving frequency, and the sum and the difference of two frequencies. Peter Franken and his colleagues sent the red light of a ruby laser, 694.3 nanometers, through a

crystal of quartz in 1961 and found ultraviolet light at half the wavelength, 347.2 nanometers, twice the frequency (Franken, Hill, Peters and Weinreich, 1961). Franken's doubling of the ruby light was the first *second-harmonic generation*. The green light of a common laser pointer is made the same way, from infrared light of 1,064 nanometers doubled to 532 nanometers in a crystal with no center of symmetry (standard accounts of lasers).

So we now know what matter does to light that drives it hard. The hold on its electrons is then not in proportion to their displacement, so they send out frequencies that were not driven. Every material sends out triples and sums of three, and where the hold is not symmetric about the electron's place, doubles, sums and differences of two.

XIII. Light Multiplied

At the end of a concert, a few people begin to clap in time, and the more who clap in that rhythm, the more readily each newcomer joins it, until the whole hall claps as one. Chapter 1, Box 1.2, showed that photons, being bosons, are not excluded, a boson being a particle whose spin is a whole number: any number of photons can share one state. Chapter 2, Section XII, described bosons as campers who crowd onto one spot. How does an atom ready to give out light behave when light of its own frequency is already passing?

Take atoms with two levels, the upper one higher by the energy hf of a photon of frequency f. An atom in the upper level can fall to the lower one and give out a photon, and an atom in the lower one can take up a photon and rise. Albert Einstein asked in 1917 how fast each must happen if atoms and light are to come to balance at a temperature, and found that the answer is fixed (Einstein, 1917). Box 11.3 follows his argument.

Box 11.3. Einstein's n + 1

Premises. (1) In balance at temperature T, atoms in the upper level are fewer than atoms in the lower one by the *Boltzmann factor*, $e^{-E/kT}$ with E = hf the difference of their energies, the weight with which a part of a system at temperature T takes a state of energy E (Chapter 2, Section X): $N_2/N_1 = e^{-hf/kT}$, with N_2 and N_1 the numbers of atoms in the upper and lower levels, each level taken as a single state. (2) In balance at temperature T, each state of light of frequency f holds on average $n = 1/(e^{hf/kT} - 1)$ photons, the Bose-Einstein distribution for photons (Chapter 2, Section XIII and Box 2.5). (3) In balance, for each state of light, photons are taken up from it as often as they are given out into it (standard statistical mechanics). (4) An atom in the lower level takes up a photon from a state of light at a rate B times the number n of photons in it; an atom in the upper level gives a photon out into that state at a rate that may depend on n, written A' + B'n, with A', B and B' fixed by the atom (the most general form to first order in n, as Einstein took it).

Steps. By (3) and (4), $N_1Bn = N_2(A' + B'n)$. By (1), $N_1/N_2 = e^{hf/kT}$, so $n = A'/(Be^{hf/kT} - B')$. By (2), $n = 1/(e^{hf/kT} - 1)$, and the two agree at every temperature only if B' = B and A' = B. So an atom in the upper level gives out a photon into a state that holds n photons at the rate B(n + 1), and an atom in the lower level takes one up from that state at the rate Bn. The same factor comes from the amplitudes of light: adding one photon to a state that holds n has the amplitude $\sqrt{(n + 1)}$, so the weight n + 1 (standard quantum mechanics of light).

Result. The rate of giving out a photon into a state of light that already holds n photons is in proportion to n + 1. The 1 is *spontaneous emission*, which happens with no light present; the n is *stimulated emission*, giving out into a state in proportion to the photons already in it, each new photon in the same state as those already there. Taking up a photon is in proportion to n, with the same constant, so light passing through atoms gains by stimulated emission in proportion to the atoms in the upper level and loses by absorption in proportion to the atoms in the lower one.

So a passing photon raises the probability that an excited atom gives out a photon, and the photon it gives out goes into the passing photon's own state: the same frequency, the same direction, the same polarization and the same phase. Light passing through atoms grows if more of them are in the upper level than in the lower, since the stimulated gains then outweigh the losses to absorption. Having more atoms in the upper level than in the lower is *population inversion*: more atoms ready to fall than ready to rise. In balance at any temperature the upper level holds fewer atoms than the lower, by (1), so light passing through matter in balance is always weakened, and inversion must be made by pumping energy in.

Atoms of three or four levels make inversion possible. In atoms of only two levels, light shining on them raises and lowers atoms at the same rate, by Box 11.3, and at best makes the two levels equally full. So lasers use three or four levels. In a three-level laser, light pumps atoms from the ground level to a high level, from which they fall quickly to a middle level that is *metastable*. A metastable state lasts far longer than the states around it because the fast way down is closed to it (Volume One, Chapter 7, Section VII). More than half the atoms must be raised before the middle level holds more than the ground level, and light of the middle level's fall then grows. Theodore Maiman's first laser of 1960 was a three-level laser, a rod of ruby, aluminum oxide with a little chromium, pumped by a flash lamp, giving red light of 694 nanometers in pulses (Maiman, 1960). In a four-level laser the light is given out in a fall to a level above the ground level, which empties at once, so even a few atoms in the upper level make an inversion. The helium-neon laser, first run by Ali Javan, William Bennett and Donald Herriott in 1960 (Javan, Bennett and Herriott, 1961), and most lasers since work this way.

Inversion makes light grow as it passes, and mirrors make it grow into one state. Two mirrors face each other at the ends of the inverted material, one of them letting a little light through, and send the light back and forth many times. On each pass stimulated emission adds photons to the states that the mirrors keep, until a few states hold almost all the light: the mirrors make an *optical cavity*. The light that leaves through the partly clear

mirror is laser light, and the whole device is a *laser*, from light amplification by stimulated emission of radiation. Its light is of one frequency, traveling in one direction, with a phase held over great distances. That keeping of one phase over the length and breadth of the beam is the light's *coherence*. Coherence lets laser light be focused to a spot near its own wavelength, travel to the Moon and back as a narrow beam, and lay down fine stripes where two of its beams cross. The maser of Volume One, Chapter 8, In Use, an amplifier of microwaves by atoms passing together from an upper level to a lower one, came first. Charles Townes, James Gordon and Herbert Zeiger ran one with ammonia molecules in 1954 (Gordon, Zeiger and Townes, 1954), and Townes, Nikolay Basov and Aleksandr Prokhorov shared the Nobel Prize in Physics for 1964. The semiconductor laser of Chapter 7, Section VI, is the light-emitting diode made with mirrors at its ends. Forward bias fills the junction with electrons above holes, an inversion, and the polished ends of the crystal make the cavity; Robert Hall ran the first, of gallium arsenide, in 1962 (Hall et al., 1962).

So we now know how light is multiplied. Photons are not excluded, and an excited atom gives out a photon into a state that holds n photons at a rate in proportion to n + 1, the 1 spontaneous and the n stimulated, while absorption goes as n, as Einstein's balance requires. So where more atoms are ready to fall than to rise, light grows as it passes, all in one state, and three or four levels and a pair of mirrors make a laser.

In Use

Nearly all the long-distance traffic of the world's telephones and computers travels as light in optical fibers, threads of glass that hold light in their cores by total internal reflection (Section V). Charles Kao and George Hockham argued in 1966 that glass made pure enough would carry light for kilometers with little loss (Kao and Hockham, 1966). The first fiber to do so was made in 1970, losing 17 decibels in each kilometer,

a loss of 10 decibels being a fall of the light to a tenth (standard accounts of optical fibers); Kao received the Nobel Prize in Physics for 2009. A modern fiber of pure silica loses about 0.2 decibels in each kilometer for infrared light near 1,550 nanometers, so that after 100 kilometers a hundredth of the light is left (computed). Along the way, lengths of fiber with a little erbium in them, pumped into inversion by a laser, amplify the light by stimulated emission (Section XIII) without turning it into an electric signal (standard accounts of optical fibers). The core and the glass round it, its cladding, differ in index by less than one percent, about 1.4475 against 1.444, so the light meets the boundary at a grazing angle beyond the critical one.

Every lens in a camera, a pair of glasses or a microscope is made by the bending of Section V, its curved faces turning each ray by Snell's law so that the rays from one point meet again at one point. Its glasses are chosen in pairs so that their dispersions (Section VI) cancel and the colors meet together. Each bare glass face sends back about four percent of the light (Section V), so a camera lens of many faces would lose much of its light and fill its pictures with stray reflections. A thin coating on each face, a quarter of a wavelength thick, sends back a second reflected wave half a cycle behind the first, and the two cancel. A coating of magnesium fluoride, of index 1.38, 100 nanometers thick, cuts the reflection of a crown-glass face from 4.3 to 1.3 percent at the middle of the visible range (computed), and coatings of many layers cut it far further (standard optics).

Polarizing sunglasses hold a polarizer that passes light swinging up and down and stops light swinging side to side, the glare reflected from water and roads near Brewster's angle (Section VIII). The screens of watches, telephones and computers that are liquid-crystal displays set each small region light or dark by turning the polarization of the light between two polarizers (Section VIII).

Lasers do work that no other light can. In surgery, the ultraviolet light of an argon fluoride laser, of 193 nanometers, reshapes the cornea of the eye by removing a fraction of a micrometer of tissue with each pulse, without heating what lies around it (standard accounts of lasers). In man-

ufacturing, the infrared light of carbon dioxide lasers, of 10.6 micrometers, cuts and welds steel, and the ultraviolet light of other lasers prints the patterns of computer chips (standard accounts of lasers). In measurement, laser light of one frequency is a ruler whose marks are its wavelengths. Interferometers, instruments that split a beam and bring its parts back together so that their crests add or cancel, count wavelengths to measure lengths and their changes. The interferometers that found gravitational waves, ripples in the shape of space and time that carry energy away (Volume One, Chapter 6, Section VI), measured with laser light the stretching of arms four kilometers long (Abbott et al., 2016). And the semiconductor lasers of Chapter 7 read optical disks and send the signals of the fibers above.

Summary

Light in matter is light and matter's re-radiated light added together, each part at c, the sum behind. A passing wave sets every bound electron swinging at the wave's frequency, and each electron sends out a wave of its own. The wave sent out by a thin sheet of such electrons is a quarter cycle behind the wave that drives them (Box 11.1). The sum of the entering wave and all those waves has its crests delayed, so its phase advances at c/n, while every part of it travels at c. So the slowing of light in matter is a sum of waves each at the unchanged speed of light, and the invariance of c stands. Near a natural frequency the matter takes up the light, its strength falling as the exponential of the thickness, and objects take their colors from what they take up. Above it the phase can advance faster than c, but the front of every change travels at c, and the index and the absorption are tied by the Kramers-Kronig relations. A charge faster than c/n trails a cone of Cherenkov light.

At a surface the wave has one phase at each place, reached from either side, so the crests on the two sides must meet. So light bends by Snell's law, toward the side where the phase advances more slowly (Box 11.2,

Figure 11.1). The surface's driven electrons send part of it back, about four percent at glass, and from inside, beyond the critical angle, no wave on the far side can match the phase, so all of it turns back, which keeps light in an optical fiber. The electrons' lag depends on how near the frequency is to the natural ones, so colors part, violet bent most. Air molecules, small against light because α is small, scatter as the fourth power of the frequency, so the sky lit from the side is blue and the low sun red. The dipole pattern, nothing sent along a charge's line of swing, polarizes the sky's light and sets Brewster's angle. Light has two polarizations for each direction of travel, chosen as linear or as circular, and no third, since light is never at rest and so has no third way of turning to be carried into. Crystals not alike in every direction slow the two linear polarizations differently and split a beam. Chiral molecules slow the two circular polarizations differently and so turn the plane of linear polarization, the mirror-image molecule turning it the other way. A metal's free electrons send back light below their plasma frequency, set by their number in each unit of volume, their charge and their mass, and let it pass above; copper and gold take their colors from their d bands.

I found three main results in this chapter, and I give each result with what that result follows from. The slowing in matter is a sum of waves each at c, which follows from the driven electrons' waves being a quarter cycle behind the waves that drive them, so the invariance of c stands. Light passes through light unchanged through the electromagnetic field, which follows from the photon carrying no charge, so that the field is linear. Light acts on light through two things and nothing else: through charges, and through gravitation. Through charges it acts in matter, where strong light makes new frequencies, triples in every material and doubles where the hold on the electrons is not symmetric, and in empty space through pairs of charged particles that briefly appear and vanish, which ATLAS saw in 2017 and 2019. Through gravitation it acts because light shapes the geometry it follows. And light multiplies, which follows from photons not being excluded. A passing photon raises the probability that an excited atom gives out a photon into the passing photon's state, in pro-

portion to n + 1 by Einstein's balance, so where more atoms are ready to fall than to rise, light grows as it passes, all in one state: the laser. The indices, the natural frequencies and the strengths of the electrons' answers to light are values of each material, and they are measured.

Throughout this chapter the nucleus has sat at the center of every atom, its charge binding the electrons that light drives. Nothing it does has entered this chapter's account, since its mass is thousands of times the electron's and its size a hundred-thousandth of the atom's. Light, magnets and currents all deal with the electrons, the rung of atoms and their electrons answering, and the rung beneath kept out of sight. The nucleus is almost hidden inside its atom. Where does it show through?

✶

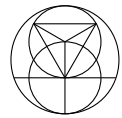
KEY CONCEPTS

- **Wavelength; frequency; phase velocity.** The distance from one crest of a wave to the next; the number of crests that pass a point in each second; and the speed at which the crests move, the wavelength times the frequency.
- **Refractive index.** The ratio n of the speed of light c to the speed at which the phase of light advances in a material: 1.333 for water, about 1.5 for glass, 2.417 for diamond.
- **Optics.** The study of light and of what matter does to it: its slowing, bending, parting, scattering, polarization and multiplying.
- **Lorentz oscillator model; re-radiated (scattered) waves.** Each bound electron taken as a charge on a spring with natural frequencies of its own; and the waves its swinging sends out at the frequency that drives it.
- **Dipole pattern.** A swinging charge sends out light most strongly at right angles to its swing and nothing along it.
- **Ewald-Oseen extinction theorem.** Inside matter, the waves of the driven electrons cancel the entering wave and build in its place a wave whose phase advances at c/n, every part traveling at c.

- **Clausius-Mossotti relation.** $(n^2 - 1)/(n^2 + 2) = N\alpha_p/(3\varepsilon_0)$, the index of a dense material from the polarizability of its molecules.
- **Absorption; Beer-Lambert law.** Matter taking up light near its natural frequencies; and the fall of the light's strength as the exponential of the thickness.
- **Group velocity; front.** The speed of a pulse's envelope; and the first part of a change of light to arrive, which travels at c in every material.
- **Kramers-Kronig relations.** Formulas, following from nothing answering before it is driven, that tie a material's index at every frequency to its absorption at every frequency.
- **Cherenkov radiation.** The cone of light trailing a charged particle that moves through matter faster than c/n.
- **Refraction; Snell's law.** The bending of light at a surface, toward the side where its phase advances more slowly: $n_1 \sin\theta_1 = n_2 \sin\theta_2$, from the crests matching along the surface.
- **Fresnel reflection.** The share of light sent back at a surface, $((n-1)/(n+1))^2$ straight on, 4 percent at glass.
- **Critical angle; total internal reflection; evanescent wave.** The angle, with sine n_2/n_1, beyond which no wave on the far side can match the phase; the turning back of all the light; and the field reaching a fraction of a wavelength past the surface, carrying nothing away.
- **Optical fiber.** A glass thread whose core holds light by total internal reflection.
- **Dispersion; Cauchy and Sellmeier formulas.** The change of the index with the frequency of the light, which parts colors; and the forms in which the index is written, a constant with a term in one over the wavelength squared, and a sum of one term for each natural frequency.

- **Rayleigh scattering; Mie scattering; Tyndall effect; Raman effect.** Scattering by particles small against the wavelength, as the fourth power of the frequency; by particles as large as the wavelength or larger, alike for every color; by colloids, making a beam visible from the side; and with a change of frequency by a molecule's vibration.
- **Polarization; linear and circular.** The direction of the swing of light's electric field, at right angles to its travel, with two independent polarizations for each direction of travel; chosen as two lines at right angles, or as the field turning clockwise and counterclockwise.
- **Birefringence.** Double refraction: a crystal not alike in every direction slows the two linear polarizations differently and splits a beam in two.
- **Brewster's angle.** The angle, $\tan \theta_B = n_2/n_1$, at which only the polarization across the plane of incidence is reflected, because the driven electrons send nothing along their line of swing.
- **Polarizer; wave plate; liquid-crystal display.** A sheet passing one linear polarization; a birefringent plate putting one polarization a quarter cycle behind the other; and a screen setting each region light or dark by turning polarization between two polarizers.
- **Chiral; optical activity; circular dichroism; Faraday rotation.** Not the same as its mirror image; the turning of the plane of linear polarization by a chiral material, which slows the two circular polarizations differently; the unequal taking up of the two; and the turning of the plane by a magnetic field, in any material.
- **Plasma frequency; skin depth.** $\omega_p = \sqrt{(Ne^2/(\varepsilon_0 m_e))}$, set by the number N of free electrons in each unit of volume, their charge and their mass, below which a metal sends light back and above which it passes it; and the depth, about c/ω_p, to which light reaches into a metal below it.
- **Linear (of the field's laws).** Any two waves the laws allow, added, make a third, each going on as it would alone; so through the field alone two beams pass through each other unchanged.

- **Nonlinear optics; second-harmonic generation; Kerr effect.** Light at frequencies the driving light did not have, from a hold not in proportion to displacement; light at twice the driving frequency, in crystals with no center of symmetry; and an index changing with the light's strength, in every material.
- **Spontaneous and stimulated emission.** An excited atom giving out a photon with no light present; and giving one out into a state of light in proportion to the photons already in it, the new photon in the same state.
- **Einstein's n + 1.** The rate of giving out a photon into a state that holds n photons is in proportion to n + 1, and of taking one up in proportion to n (Box 11.3).
- **Population inversion; three- and four-level lasers.** More atoms ready to fall than ready to rise, which makes light grow as it passes; and the schemes of levels by which pumping reaches it.
- **Optical cavity; laser; coherence.** Two facing mirrors that keep light passing through an inverted material; the device that makes light by light amplification by stimulated emission of radiation, its light of one frequency in one direction; and the keeping of one phase over the beam.



Chapter 12

The Nucleus Seen in Matter

CHAPTER OVERVIEW

Inside its atom the nucleus is almost hidden: it nearly stays where it is while the electrons move, and the electrons answer mostly to its charge. In this chapter I find the places where it shows through all the same: in atoms, molecules, crystals, decays and clocks. Isotopes of one element have the same nuclear charge, so their electrons, their shells and their bonds are almost the same. They differ in four ways. The first way that isotopes differ is the small motion of the nucleus, which shifts the atom's levels by about the electron's mass over the nucleus's. The second way that isotopes differ is the size of the nucleus, which shifts the electron states that reach into the nucleus. The third way that isotopes differ is the least motion that an atom held in a bond or a crystal keeps even at the lowest temperature, the atom's zero-point motion, whose energy goes as one over the square root of the atom's mass. So a heavier isotope sits lower in its bond, holds it more strongly and reacts more slowly. The fourth is everything that goes with the atom's motion: its wandering through a gas, its carrying of heat and, in a metal, the temperature at which its electrons pair. Nucleons of one kind pair with opposite spins. So a nucleus with every nucleon paired has spin zero, and a nucleus with one unpaired nucleon always has a spin of one half or more. A nucleus with one unpaired proton and one unpaired neutron usually has a spin of one or more, and their spins can also cancel. A nucleus with spin is a small magnet, far weaker than the electron, since the natural unit of its

moment is smaller than the electron's by the ratio of the masses, 1836. In a magnetic field its orientations differ in energy in proportion to the field, because the field's laws are linear. It takes up radio waves at the frequency that matches the difference, 42.58 megahertz in each tesla for hydrogen (Box 12.1): nuclear magnetic resonance. The electrons, driven round by the field, change the field the nucleus meets, mostly by opposing it, so the frequency reports the chemical surroundings, while nuclei with every nucleon paired, such as carbon-12 and oxygen-16, are silent. A free nucleus that gives off a gamma ray recoils, and the gamma ray falls short of what an identical nucleus needs to take it up (Box 12.2). In a crystal, whose vibrations come in quanta, the whole crystal can take the recoil when no vibration is made. Then the gamma ray is given and taken up with its natural sharpness (Box 12.3), sharp enough to read the shift of frequency that gravitation makes over 22.5 meters of height. Most decays are set inside the nucleus, which lies far inside its atom by the ordering of the masses, so the electrons scarcely touch them. A few decays deal with an electron of the atom: in electron capture the nucleus takes in one of its own electrons, and in internal conversion it hands its energy to one, which flies out. Both depend on how much of an electron's state reaches the nucleus, which the chemical form changes slightly. A stripped atom, one with every electron taken away, cannot capture an electron at all, and a stripped atom stable when whole can decay by placing its new electron in an empty bound state. And atoms of one kind cannot be told apart, so the frequency of any of their transitions is the same for every such atom everywhere in the universe, which makes it a standard of time (Box 12.4). Cesium defines the second today, and clocks built on transitions of light, which swing far faster than cesium's microwaves, now surpass it.

I. A Scanner That Sees the Nucleus

Chapter 11 ended with a question: the nucleus is almost hidden inside its atom, so where does it show through?

A patient lies still inside the long tunnel of a hospital scanner, and for half an hour the machine knocks and hums. At the end of it a doctor looks at pictures of the patient's brain, slice by slice, in which the gray matter, the white matter and the fluid between them stand out from one another, though no knife and no X-ray has touched the patient. The pictures are made from radio signals given out by the nuclei of the hydrogen in the patient's body: the protons at the centers of the hydrogen atoms of the water and the fat. Yet all of chemistry, the joining of atoms of Volume One, Chapter 11, and the bands, magnets and light of this volume, has gone on as if the nucleus were a point of charge and nothing more.

So the reader's question is this: if chemistry ignores the nucleus, how does a hospital scanner see it?

The *nucleus* is the atom's small, dense core, made of protons and neutrons, which are together called nucleons (Volume One, Chapter 1, Section I). It hides inside its atom for two reasons, both found in Volume One. First, it is heavy: a proton has 1836 times the electron's mass, and every other nucleus more, so in the atom the nucleus nearly stays where it is while the electrons move (Volume One, Chapter 7, Section IX). Second, it is small: a nucleus is a few femtometers across, a femtometer being 10^{-15} meters. A hydrogen atom is some sixty thousand times wider than its proton (Volume One, Chapter 1, In Use, from the Bohr radius, 0.529×10^{-10} m, against the proton's 0.84 fm). So the electrons answer, almost wholly, to one thing about the nucleus: its charge. The levels of an atom, the order of the periodic table and the bonds between atoms are all set by that charge, and the rest of the nucleus is hidden behind it.

Almost wholly is not wholly, and in the rest of this chapter I find where the nucleus shows through. It shows in the differences between isotopes, atoms whose nuclei have the same charge and different masses and sizes (Sections II to V). It shows in the magnetism of nuclei with spin, a nucleus's angular momentum in itself, which the hospital scanner reads (Sections VI to IX). It shows in the gamma rays that nuclei give off and take up, which a crystal can make exact (Sections X to XII). It shows in the

few decays that the electrons around a nucleus can slow, stop or start (Sections XIII and XIV). And it shows in clocks: the nucleus's magnet splits the atom's lowest level, and the frequency of that splitting is a standard of time (Section XV).

II. Isotopes: Alike in Their Bonds, Different in Four Ways

Freeze a little heavy water, water whose hydrogen atoms each carry a neutron beside the proton, and drop the ice cube into a glass of ordinary water. It sinks. Heavy water looks like water, tastes almost like water and dissolves what water dissolves. Yet a liter of it weighs about 1.107 kilograms, more than ordinary water by about a tenth, it freezes at 3.82 degrees Celsius and it boils at 101.4 degrees (standard tables of the properties of heavy water). How can two waters be so alike and still not the same?

Different forms of one element, with the same number of protons and different numbers of neutrons, are its *isotopes* (Volume One, Chapter 7, Section IX). Hydrogen has two that last: ordinary hydrogen, whose nucleus is one proton, and *deuterium*, heavy hydrogen, whose nucleus is a proton and a neutron bound together, about twice the proton's mass. In the ocean about one hydrogen atom in 6,400 is deuterium, 156 for each million (standard tables of the abundance of deuterium). The nuclei of two isotopes have the same charge, so the electrons of the two atoms meet the same pull. In Volume One, Chapter 11, Section XVI, I found what follows: the electrons' energy depends on the nuclei's charges and places, and not on their masses. So the electrons of two isotopes take the same states, fill the same shells and make the same bonds, and isotopes join almost alike. The hydrogen molecule H_2 needs 4.478 eV to be pulled apart, and D_2, made of two deuterium atoms, 4.556 eV (Volume One, Chapter 11, Section XVI): the same bond, differing by less than two percent. So chemistry can ignore the nucleus: the chemistry of an atom depends only on the nucleus's charge, and isotopes share that charge.

The word "almost" is where the nucleus shows through, and it shows in four ways, which I follow in turn in the next three sections. The first of the four ways is the nucleus's own small motion: the nucleus nearly stays where it is, but not quite, and how far it moves depends on its mass (Section III). The second of the four ways is the nucleus's size: isotopes with more neutrons have larger nuclei, and the electron states that reach into the nucleus feel the difference (Section III). The third of the four ways is the least motion of the whole atom held in a bond or a crystal, the atom's zero-point motion, which depends on the atom's mass (Section IV). The fourth is everything else that goes with the atom's motion: how fast it wanders through a gas, how it carries heat through a crystal, and, in a metal, how the lattice it is part of pulls electrons into pairs (Section V). The ice cube that sinks shows the third and fourth: the heavy water molecule is heavier by the mass of two neutrons, and its hydrogen bonds are a little stronger, for the reason Section IV gives, so it melts at a higher temperature.

So we now know why isotopes are chemically almost the same: their nuclei have the same charge, and the electrons, which make every bond, answer to the charge and not to the mass. They differ in four ways, all of them through the nucleus's mass or size: the nucleus's own motion, its size, the atom's zero-point motion in a bond or crystal, and whatever else goes with the atom's motion.

III. The Nucleus Moves a Little, and Has a Size

In Volume One, Chapter 7, Section IX, I set a grown man and a small child face to face on ice skates and let them push apart: both move, and the heavier one moves less. In an atom the nucleus is the man and the electron the child. Put a heavier man on the skates, and he moves less still. How does an atom's light tell which isotope its nucleus is?

The first way is the nucleus's motion. The electron and the nucleus turn about their common center of mass. So the exact account of the atom replaces the electron's mass, wherever it enters, by the *reduced mass*, $m_e M/(m_e + M)$ for a nucleus of mass M, the electron's mass made smaller by about one part in M/m_e (Volume One, Chapter 7, Section IX, where M is the proton's mass and the part is one in 1836). Every level's energy is in proportion to the reduced mass, so a heavier nucleus, which moves less, gives slightly deeper levels and light of slightly higher frequency. The levels of two isotopes, of masses M_1 and M_2, therefore differ by a share of about $m_e(1/M_1 - 1/M_2)$, the electron's mass over the nucleus's taken for each isotope and subtracted: the *normal mass shift*. For hydrogen against deuterium the share is about half of 1/1836. So the red Balmer line of deuterium lies 0.18 nanometers to the blue of hydrogen's, which is how Harold Urey and his colleagues found deuterium, at the end of 1931 (Urey, Brickwedde and Murphy, 1932; Volume One, Chapter 7, Section IX; 0.179 nm computed). For heavier atoms the share is far smaller: between calcium-40 and calcium-48 it is about two parts in a million (computed).

In an atom with many electrons the nucleus moves against all of them at once. Its momentum is the sum of theirs, reversed, and its energy of motion is the square of that sum over twice its mass. The square of a sum holds the square of each part and a product for every pair of parts, as $(a + b)^2$ holds a^2, b^2 and 2ab. The square of each electron's own momentum is the part the reduced mass already counts. The product for each pair of electrons is new: it adds energy when the two tend to move the same way at the same moment and takes energy away when they tend to move opposite ways, so it depends on how the electrons' motions are correlated with one another. That further part is the *specific mass shift* (Hughes and Eckart, 1930). It can raise or lower a level, and in some atoms it is as large as the normal one (standard atomic physics). Both parts go as one over the nuclear mass, so both fall as the nuclei grow heavier.

The second way is the nucleus's size. In Volume One, Chapter 8, Sections V and VIII, I found that only the S states, the states of no orbital angular momentum, reach the center of the atom. I found too that inside a nucleus of finite size the electric pull is weaker than the pull of a point charge, so the S states are lifted by an amount that goes as the square of the nucleus's size. For a charge Z shared over a sphere, the S state's level rises by $(2\pi/3)(Ze^2/(4\pi\varepsilon_0))|\psi(0)|^2\langle r^2\rangle$ (Volume One, Chapter 8, Box 8.3, premise 3, written for a nucleus of charge Z; standard atomic physics). Here $|\psi(0)|^2$ is the weight of the electron's state at the center, and ε_0 is the electric constant, the number that sets, in the international units, how strong a field a given charge makes (Chapter 4, Section IX). And $\langle r^2\rangle$ is the mean square radius of the nuclear charge, the average of the square of the distance from the center over all of the nucleus's charge. Isotopes with more neutrons have larger nuclei, since a nucleus's radius grows as the cube root of its number of nucleons, about $1.2\ A^{1/3}$ femtometers (Volume One, Chapter 4, Section VI). So the S states of two isotopes are lifted by different amounts, in proportion to the difference of their mean square radii: the *field shift*, also called the volume shift. The field shift grows steeply with the nuclear charge, both through the charge Z and because an inner electron of a heavy atom crowds close to its nucleus. That electron's weight at the center grows as Z^3, since its size is a_0/Z (Volume One, Chapter 9, Section II). So in light atoms the mass shift is the larger, and in heavy atoms the field shift is.

Measured shifts hold both parts together, and they are taken apart by comparing two lines. For each pair of isotopes, both lines have a mass part in proportion to the same factor of the masses and a field part in proportion to the same difference of mean square radii, each line with its own two constants. Divide each line's shift by the factor of the masses for that pair. Then each divided shift is the line's own mass constant plus the line's own field constant times one number belonging to the pair: the difference of radii divided by the factor of the masses. That number changes from pair to pair, but both lines share it, so each time it grows, the divided shift

of the second line grows by a fixed multiple of the growth of the first's. So when the divided shifts of the two lines are set against each other for several pairs of isotopes, the points fall on a straight line, a *King plot* (King, 1963). Its slope is the ratio of the two lines' field constants, and where it crosses the axis is set by their mass constants, so its slope and intercept give the two parts. From the field parts come the differences of the nuclei's charge radii, isotope by isotope, measured with light that never enters the nucleus except through the S electrons' small share of time there.

So we now know two ways an atom's light tells its isotope. The nucleus moves a little with its electrons, by an amount set by its mass, which shifts every level by about the electron's mass over the nucleus's, with a further part from the correlated motions of many electrons. And the nucleus has a size, which lifts the S states, the only ones that reach it, by an amount set by its mean square radius. The mass shift rules in light atoms, the field shift in heavy ones, and the two are taken apart by comparing lines.

IV. Heavier Atoms Sit Lower in Their Bonds

In Chapter 3, Section VI, I hung a light weight and a heavy one from two springs of the same stiffness and set both bouncing: the heavy one bounces more slowly. A bond is such a spring, and an isotope is a heavier weight on the same spring. The mass shift of Section III is a few parts in a million for most atoms. Is that all the nucleus's mass can do?

The mass does far more, because a whole atom moves as well as its electrons. An atom held in a bond, or at its place in a crystal, is confined, and a confined thing has a least energy of motion that it cannot give up, since confinement always costs energy (Volume One, Chapter 7, Section IV). For a vibrating bond that least energy is half a quantum of the vibration, hf/2, with f its frequency, the *zero-point energy* (Chapter 3, Section VI; Volume One, Chapter 11, Section XVI). The zero-point energy of a bond comes from the same mathematics as for any confined thing with a least state, applied to the confinement that the bond itself provides. The bond's

stiffness, K, is made by the electrons, which answer to the nuclei's charges and not their masses, so it is the same for every isotope. The frequency of a weight M on a spring of stiffness K goes as $(K/M)^{1/2}$, with M here the reduced mass of the pair the bond joins. So the zero-point energy of a held atom goes as one over the square root of its mass.

Three consequences follow, each the same fact read another way. A heavier isotope sits lower in its bond: its curve of energy against separation is the same, since the electrons are the same, but it keeps less energy at the bottom of that curve. Its bond therefore takes more to break: the energy to pull a molecule apart is the depth of the curve less the zero-point energy, and the smaller zero-point energy of the heavier isotope leaves more to supply. D_2, whose vibration is 0.708 times as fast as H_2's (Huber and Herzberg, 1979), needs 4.556 eV to be pulled apart against H_2's 4.478 eV (Volume One, Chapter 11, Section XVI). H_2's zero-point energy is about 0.27 eV, and 0.27 eV times $(1 - 0.708)$ is 0.079 eV, against the measured difference of 0.078 eV (computed). And a reaction that breaks the heavier isotope's bond, or moves the heavier atom across its barrier, is slower.

That last consequence is the *kinetic isotope effect*, the slower reaction of a heavier isotope, from its lower zero-point energy and, where tunneling plays a part, from its smaller tunneling (Chapter 3, Section VI). Over the barrier, the barrier measured from where the bond starts is higher for the heavier isotope by the difference of the two zero-point energies. So its rate is lower by the Boltzmann factor of that difference: for a bond of carbon to hydrogen against the same bond to deuterium, up to about seven times at room temperature (Chapter 3, Section VI; Westheimer, 1961). Through the barrier, the share that passes falls as the exponential of the square root of the mass (Chapter 3, Section III), so where tunneling carries part of the reaction, doubling the mass cuts it by far more, and the ratio is larger than seven. The effect is largest for the lightest atoms, where the ratio of the masses is largest: deuterium has twice hydrogen's mass, but carbon-13 has only 13/12 of carbon-12's, and its reactions are slowed by a few percent at

most (standard accounts of kinetic isotope effects). So hydrogen against deuterium is the isotope effect chemists use most, and the size of the slowing tells them which bond a reaction breaks in its slowest step.

The zero-point energy works the same way for an atom at its place in a crystal. Each atom of a crystal is held by its neighbors as if by springs, and the lattice's vibrations come in quanta, the phonons, a phonon being a quantum of vibration of a crystal's lattice (Chapter 5, Section IV). A crystal of a heavier isotope vibrates more slowly in every one of its modes, by one over the square root of the mass, with a lower zero-point energy for each atom.

So we now know the third way isotopes differ. A held atom, in a bond or a crystal, keeps a zero-point energy that goes as one over the square root of its mass, since the electrons make the same spring for every isotope. So a heavier isotope sits lower in its bond, holds it more strongly, and reacts more slowly, most of all where the mass ratio is largest, for hydrogen against deuterium.

V. Heavier Atoms Move More Slowly, and Pair Later

In Chapter 7, Section III, I let perfume reach the next room through an open door, its molecules wandering from where they were many to where they were few. A perfume of heavier molecules would take longer, because in a gas at one temperature the light molecules dart and the heavy ones amble. What else goes with the atom's motion, and does it have the same cause as the zero-point energy of Section IV?

The rest of what goes with the atom's motion has a different cause from the cause of the zero-point energy, and the difference between the two causes matters. In a gas at temperature T, every molecule holds on average 3/2 kT of energy of motion, whatever its mass. The same average energy of motion for every molecule, whatever the molecule's mass, is *equipartition* (Chapter 2, Section X). Equipartition is the rule that an energy going as the square of a velocity holds on average ½kT for each direc-

tion of motion, when kT is large against the quanta of that motion. So $\frac{1}{2}Mv^2$ is the same on average for every kind of molecule, and the typical speed goes as one over the square root of the mass. That square root comes from the counting of ways at a temperature, with no quantum in it. The square root of Section IV comes from the quantum of a vibration on a spring the electrons make. Both say that a heavier isotope moves more slowly, by the square root of the mass ratio, but they say it of different motions for different reasons.

The first consequence of the slower motion is *diffusion*, the wandering of particles, by their random motion, from where they are many to where they are few (Chapter 7, Section III). A gas leaking through a wall of fine pores, too fine for the gas to flow through as a whole, passes molecule by molecule, at a rate in proportion to the molecules' speed. So the lighter isotope leaks faster by the square root of the ratio of the masses: *Graham's law*, found by Thomas Graham in the nineteenth century (standard physical chemistry). Graham's law is the basis of separating isotopes by gaseous diffusion. Uranium is made into the gas uranium hexafluoride, whose molecules carrying uranium-235 and uranium-238 have masses of 349.03 and 352.04 atomic mass units, the atomic mass unit being a twelfth of the mass of an atom of carbon-12 (Chapter 2, Section X). One pass through a porous wall enriches the lighter molecule by the factor $(352.04/349.03)^{1/2} = 1.0043$ (computed). So a diffusion plant needs well over a thousand passes in a row to enrich uranium for a reactor (standard accounts of isotope separation).

A centrifuge separates isotopes by another law. In a gas spinning at the speed v at the wall of a tube, each molecule is pressed outward, as a rider on a turning carousel is pressed toward its rim. To an observer turning with the gas, that outward push acts like a slope whose bottom is at the wall: a molecule of mass M has less energy at the wall than at the axis by $\frac{1}{2}Mv^2$ (standard mechanics of turning bodies). By the Boltzmann factor of that energy, the share of molecules at the wall against the share at the axis is $e^{Mv^2/2kT}$ (Chapter 2, Section X). For two isotopes the ratio of those

shares goes as $e^{\Delta M v^2/2kT}$, set by the difference of the masses, ΔM, and not by their ratio (standard physics of the gas centrifuge). For uranium hexafluoride at 300 kelvin and a wall speed of 600 meters a second, a speed of the order modern centrifuges reach, that ratio is 1.24 for each pass (computed), far more than diffusion's 1.0043. The far larger gain for each pass is why centrifuges have replaced diffusion plants (standard accounts of isotope separation).

The second consequence is the carrying of heat. In a gas, heat is carried by molecules moving from warmer places to cooler ones, so a gas of a heavier isotope, whose molecules move more slowly, carries heat more slowly. In a crystal, heat is carried by phonons, which are scattered, among other things, by atoms of other mass in the lattice (Chapter 5, Section V): a crystal of one isotope is a more perfect repeat than a crystal with its isotopes mixed. Diamond made of 99.9 percent carbon-12 carries heat through itself 50 percent faster at room temperature than diamond with the natural share of carbon-13, about one percent (Anthony et al., 1990).

The third consequence is in a metal's superconductivity. In Chapter 9, Section X, I found that heavier nuclei vibrate more slowly, which narrows the band of energy in which the pull between electrons through the lattice acts, while the pull's strength stays the same. So the transition temperature at which the electrons pair falls as one over the square root of the nuclear mass, T_c in proportion to $M^{-1/2}$. That rule, the *isotope effect* of superconductivity, was found in mercury in 1950 (Maxwell, 1950; Reynolds, Serin, Wright and Nesbitt, 1950). Its size in a metal measures how much of the pull between the metal's electrons comes through the lattice's vibrations (Chapter 9, Section X).

So we now know the fourth way isotopes differ. At one temperature every molecule holds the same energy of motion on average, by equipartition, so a heavier isotope moves more slowly by the square root of the mass ratio. It diffuses more slowly, which separates isotopes by diffusion,

and it carries heat differently. A centrifuge separates isotopes by the difference of their masses instead. And in a metal whose electrons pair through the lattice, a heavier isotope pairs them at a lower temperature.

VI. The Spin of a Nucleus

Sort a drawer of socks into pairs. If the drawer holds an even number of socks of each color, every sock finds a partner and nothing is left over. If one color has an odd number, one sock of that color is left alone, and it is the odd sock that shows. The hospital scanner reads the nuclei of hydrogen, and none at all from the carbon and oxygen that make up most of the body's mass. Which nuclei have spin, and so a magnet the scanner can read?

A nucleus's *spin* is its angular momentum in itself, with no motion along a path, as Volume One, Chapter 7, Section VI, defines spin. For a nucleus it is the sum of its nucleons' spins and their orbital angular momenta, the whole taken as one. Nucleons of one kind pair. Two protons, or two neutrons, in one level with opposite spins add to spin zero and bind more strongly than either alone, because a pull of short reach gains most when the two nucleons share one region (Volume One, Chapter 4, Sections VII and IX, the pairing term). So in a nucleus with an even number of protons and an even number of neutrons every nucleon is paired with one of its kind. Its ground state, a system's state of least energy (Chapter 1, Section VI), has spin zero (Volume One, Chapter 4, Section IX). Carbon-12, of six protons and six neutrons, and oxygen-16, of eight and eight, have spin zero, and so has every nucleus with both numbers even.

A nucleus with one nucleon unpaired has a spin of one half or more, always. Its mass number is odd, so it is made of an odd number of nucleons, each of spin one half. Angular momenta add as halves and wholes add: a whole of an odd number of particles of spin one half keeps a half, since any orbital motion of its parts adds only whole units of $\hbar$ (Volume One, Chapter 1, Section V). Its spin is therefore an odd number of halves,

1/2, 3/2, 5/2 and so on, and never zero. The proton itself has spin 1/2, and carbon-13, with one neutron beyond carbon-12's, has spin 1/2. Oxygen-17 has its odd neutron in a level of five halves, and spin 5/2 (Volume One, Chapter 4, Section IX).

A nucleus with one unpaired proton and one unpaired neutron, an odd-odd nucleus, has an even number of nucleons, so its spin is a whole number. The two unpaired nucleons, each with an odd number of halves, can add to zero or to a whole number above it. Usually they add to one or more. Deuterium, one proton and one neutron, has spin 1, with the two spins aligned (Volume One, Chapter 4, Box 4.3). Nitrogen-14, seven of each, has spin 1, and boron-10 has spin 3 (standard tables of nuclear spins). But the two spins can cancel: in the odd-odd nuclei with equal numbers of protons and neutrons from chlorine-34 to cobalt-54 (chlorine-34, scandium-42, vanadium-46, manganese-50 and cobalt-54) the ground state has spin zero. Their decays to the spin-zero nuclei below them, from spin zero to spin zero, are among the best measured of all beta decays. They give the strength of the weak interaction between the up and the down quark more exactly than any other measurement (Hardy and Towner, 2020).

So the rule for nuclear spin has three parts. One unpaired nucleon always gives a spin of one half or more. One unpaired proton with one unpaired neutron usually gives a spin of one or more, though their spins can cancel. Every nucleon paired gives spin zero.

A nucleus with spin is a small magnet. Its magnetic moment, how strong a small magnet a body is, measured by the turning push that a magnetic field of a given strength gives it (Chapter 1, Section VI), comes from its turning charge. For the same angular momentum, a moment goes as the charge over the mass. So the natural unit of a nucleus's moment is the nuclear magneton, the moment of one unit $\hbar$ of orbital angular momentum carried by a charge e with the proton's mass, $e\hbar/(2m_p)$ (Chapter 1, Section IX; Volume One, Chapter 3, Section VII). It is $5.0507837393 \times 10^{-27}$ joules for each tesla (CODATA 2022), 1/1836 of the electron's Bohr

magneton (Chapter 8, Section II). Nuclear moments are a few nuclear magnetons: the proton's is 2.793, the neutron's −1.913 and the deuteron's 0.857 (CODATA 2022). So a nucleus's moment is smaller than an electron's by about the ratio of the masses. The proton's is 1/658 of the electron's: the ratio of the masses, 1836, divided by the proton's 2.793 nuclear magnetons, and multiplied by the electron's own moment, 1.00116 Bohr magnetons (CODATA 2022; Volume One, Chapter 8, Section VII). The moment of a nucleus with one unpaired nucleon lies near the moment that nucleon would carry alone in its level, a value called its Schmidt moment (Volume One, Chapter 4, Section IX). A nucleus with every nucleon paired has no moment at all.

A nucleus of spin one or more can also have a shape that is not round, an *electric quadrupole moment*, the measure of how far its charge departs from a sphere (Volume One, Chapter 4, Section IV). The deuteron, of spin 1, has one of 0.2857 e fm^2, with e the proton's charge, and it is positive, so the deuteron is drawn out along its spin like a short cigar (Puchalski, Komasa and Pachucki, 2020; Volume One, Chapter 4, Section IV). A nucleus of spin one half has none, and the reason is a count. Every property of a nucleus that a field can read is built from its orientations, and a nucleus with n orientations has room for n × n numbers of that kind. A nucleus of spin one half, with two orientations, has room for four: one that is the same in every direction, its charge, and three that together make an arrow, its magnetic moment. A shape drawn out along an axis, alike at both ends, needs five numbers more, and only a nucleus of spin one or more, with at least three orientations and so room for at least nine numbers, can hold them (standard nuclear physics). A nucleus with a quadrupole moment feels not only the electrons' magnetic field but how their electric field changes from place to place across it, and I take that up again in Section XI.

So we now know which nuclei have spin and how strong a magnet each is. Nucleons of one kind pair with opposite spins, so a nucleus with every nucleon paired has spin zero. One unpaired nucleon always leaves a spin of one half or more. One unpaired proton and one unpaired neutron

usually leave a spin of one or more, and their spins can also cancel. A nucleus with spin carries a moment of a few nuclear magnetons, smaller than an electron's by about the ratio of the masses, and a nucleus of spin one or more can also have a shape drawn out from a sphere.

VII. Nuclear Magnetic Resonance

Spin a child's top and tilt it. It does not fall over at once: its axis swings slowly round the upright, and the harder gravity pulls on it, the faster the axis swings round. A nucleus with spin, set in a magnetic field, is a spinning magnet pulled by the field. How does a magnetic field make a nucleus answer to radio waves, and at what frequency?

The *tesla* is the unit of magnetic field, the field being the push and pull that moving charges and magnets exert on other moving charges and magnets at each place around them (Chapter 8, Section II). A nucleus's moment in a field has an energy that depends on how it points, lower along the field and higher against it, as an electron's does (Chapter 8, Box 8.1). Its angular momentum along the field comes in whole units of $\hbar$, so its energies come in separate levels too, and a photon whose energy matches the difference between two neighboring levels can be taken up. In Box 12.1 I find the size of that difference and the frequency of the matching photon.

Box 12.1. Resonance at a frequency in proportion to the field

Premises. (1) A nucleus of spin I has $2I + 1$ orientations along the direction of a field, its angular momentum along that direction being $m\hbar$, with m running from $-I$ to $+I$ by ones (Volume One, Chapter 9, Section III, for the orientations of an angular momentum; Section VI for the spin of a nucleus). (2) The nucleus's magnetic moment along that direction is $\gamma\hbar m$, where γ, read "gamma", the *gyromagnetic ratio*, is the ratio of the nucleus's moment to its angular momentum, a value of each kind of nucleus (standard nuclear physics; Section VI). (3) The energy of a moment μ in a field B, a field that the moment does not itself change, is $-\mu B$ along the field, in

proportion to the field: the laws of the electromagnetic field are linear, so the field of the magnet and the field of the nucleus add, each as it would be alone, and the energy of the nucleus in the magnet's field is the product of the nucleus's moment and the magnet's field (Chapter 11, Section XI, the field's laws linear; standard electromagnetism). (4) A photon carries one unit $\hbar$ of angular momentum, so taking up one changes m by one, and it is taken up when its energy hf, with h the Planck constant and f its frequency, matches the difference of the energies of the two orientations (Volume One, Chapter 5, Section X; Volume One, Chapter 7, Section VII).

Steps. By (2) and (3), the orientation m has the energy $E_m = -\gamma\hbar mB$. Neighboring orientations, m and $m - 1$, differ by $\gamma\hbar B$, the same difference for every pair, in proportion to the field. By (4), the photon taken up has $hf = \gamma\hbar B$, so $f = \gamma B/2\pi$. For the proton, $\gamma/2\pi$ is 42.577478461 megahertz for each tesla (CODATA 2022), so f is 63.87 megahertz at 1.5 tesla and 127.7 megahertz at 3 tesla (computed): radio waves. At 1.5 tesla the difference is $hf = 2.64 \times 10^{-7}$ eV, against $kT = 0.0267$ eV at body temperature, 310 kelvin. By the Boltzmann factor the lower of the proton's two orientations holds more nuclei than the upper by a share of about $hf/2kT$, 4.9 in a million (computed, as Chapter 8, Box 8.1, counts the electron's two orientations).

Result. A nucleus with spin in a magnetic field takes up radio waves at the frequency $f = \gamma B/2\pi$, in proportion to the field, because the energy of a moment in a field that the moment does not change is linear in the field: 42.58 megahertz in each tesla for the proton. The tiny excess of nuclei in the lower orientation, a few in a million, is what takes up more than it gives out, and so makes the signal.

That taking up of radio waves by nuclei with spin in a magnetic field, at the frequency that matches the differences of energy between their orientations, is *nuclear magnetic resonance*, called NMR. The word resonance names that matching of the frequency to the difference. The same frequency is the rate at which the top's axis would swing round. A nucleus's moment, tilted from the field, swings round the field's direction at $f = \gamma B/2\pi$, the *Larmor frequency* (standard physics), so the frequency of the

matching photon and the rate of the swing are one number seen two ways. Isidor Rabi first measured nuclear moments this way, in beams of molecules flying through a vacuum, in 1938. Felix Bloch and Edward Purcell, separately, found the resonance of nuclei in liquids and solids in 1946, for which they shared the Nobel Prize in Physics for 1952 (standard accounts of NMR; Purcell, Torrey and Pound, 1946; Bloch, Hansen and Packard, 1946).

Table 12.1. Nuclei and their resonance: spin, gyromagnetic ratio over 2π (the frequency of resonance in each tesla) and the share of the element's atoms that are of that isotope. Gyromagnetic ratios from CODATA 2022 for hydrogen-1 and from standard tables of nuclear moments for the others. Spins and shares from standard tables of nuclides. The two nuclei with every nucleon paired have spin zero and no resonance.

Nucleus	Spin	$\gamma/2\pi$ (MHz per tesla)	Share of the element
Hydrogen-1	1/2	42.577	99.98 percent
Hydrogen-2 (deuterium)	1	6.536	0.016 percent
Carbon-12	0	none	98.9 percent
Carbon-13	1/2	10.708	1.1 percent
Nitrogen-14	1	3.077	99.6 percent
Nitrogen-15	1/2	−4.316	0.4 percent
Oxygen-16	0	none	99.76 percent
Oxygen-17	5/2	−5.772	0.04 percent
Fluorine-19	1/2	40.078	100 percent
Phosphorus-31	1/2	17.235	100 percent
Iron-57	1/2	1.382	2.1 percent

A minus sign in the table means that the nucleus's moment points against its spin, as the neutron's does. The frequency is the same size either way, and the sign shows only in which way the moment swings round the field. In the strongest magnets made for chemistry, about 28 tesla, the proton's resonance lies at 1.2 gigahertz. In the 1.5 and 3 tesla magnets of hospital scanners it lies at 64 and 128 megahertz (Chapter 9, In Use, for the scanners' superconducting magnets; standard accounts of NMR and MRI).

Today the resonance is measured by a pulse. A short burst of radio waves at about the resonant frequency tips the nuclei's small excess of moment away from the field. The tipped moments then swing round the field together, at their Larmor frequencies, and their swinging induces a small voltage in a coil, which dies away as the nuclei fall out of step. The record of that dying voltage holds every frequency present at once. A calculation called the Fourier transform, which sorts a signal into the frequencies of which it is the sum, turns it into the spectrum. Richard Ernst developed this method and the spectra of two and more frequencies built on it, for which he received the Nobel Prize in Chemistry for 1991 (standard accounts of NMR).

Two times describe how the signal dies. The nuclei's tipped moments return to lie along the field, giving their small energy to the surrounding molecules, in the time T_1, the *longitudinal relaxation time*, longitudinal because it is the return of the part of the moment that lies along the field. And the nuclei fall out of step with one another, because each meets a slightly different field from its neighbors, in the time T_2, the *transverse relaxation time*, transverse because it is the loss of the part of the moment that swings across the field (standard accounts of NMR). T_2 is usually the shorter. The falling out of step can be undone in part: a second pulse that reverses the sense of every nucleus's drift brings them back into step, the spin echo of Chapter 2, Section V (Hahn, 1950; Carr and Purcell, 1954).

Both times depend on how the molecules round a nucleus move, and so on the tissue it sits in, which is what makes the pictures of the In Use section.

The electron has a resonance of the same kind. An unpaired electron, of moment one Bohr magneton, swings round a field about 658 times faster than a proton, at 28.02 gigahertz in each tesla (computed from CODATA 2022). So *electron spin resonance*, the same taking up of photons by unpaired electrons, lies in the microwaves. Yevgeny Zavoisky first saw it in 1944 (standard accounts of electron spin resonance). It finds the molecules and the flaws in crystals that hold an unpaired electron, as NMR finds nuclei.

So we now know how a magnetic field makes a nucleus answer to radio waves. In a field, the orientations of a nucleus with spin differ in energy in proportion to the field, because the energy of a moment in a field that the moment does not change is linear in that field. The nucleus takes up the photon whose energy matches the difference between neighboring orientations, at $f = \gamma B / 2\pi$, 42.58 megahertz in each tesla for hydrogen, which is also the rate at which its moment swings round the field. The signal is read from a pulse, and its dying is measured by two times.

VIII. The Electrons Change the Field the Nucleus Meets

Drop a strong small magnet down a copper pipe held upright, and it does not fall: it drifts down slowly, as if through honey, though copper is not drawn to a magnet at all. The falling magnet drives currents round the copper, and their field opposes the change that drives them. The electrons round a nucleus are charges free to move round it too. If every proton has the same gyromagnetic ratio, how can one proton's resonance differ from another's and report its chemical surroundings?

A field switched on near an atom changes the motion of all its electrons, the paired ones included, and drives them round the field's direction. The moving charges make a small current in the atom whose own

field opposes the field applied, as the currents in the copper pipe oppose the falling magnet. The atom's small current opposing the applied field is *Lenz's law*, after Emil Lenz: a current driven by a changing field makes a field that opposes the change (standard electromagnetism). Seen from outside the atom it is the *diamagnetism* of Chapter 8, Section II, by which every material is pushed slightly away from a magnet. Seen from the nucleus, the electrons' field opposes the applied field at the very center of the atom, so the nucleus meets a field slightly smaller than the magnet's: it is *shielded*. Willis Lamb computed this shielding for atoms in 1941, from the electrons' states (Lamb, 1941). The electrons' field is in proportion to the field that drives them, so the field at the nucleus is $B(1 - \sigma)$, with σ, read "sigma", the *shielding constant*, a pure number set by the electrons' states, and the resonance falls at $\gamma B(1 - \sigma)/2\pi$.

In a molecule there is a second part, with the opposite sign. The electrons of a lone atom, in a state that is round, can turn freely round the field, and that turning is the opposing current. The electrons of a molecule are not free to turn so, since the bonds hold them in shapes that are not round. Instead the field mixes into the molecule's ground state a little of its higher states, states in which the electrons go round the nucleus as a current. Of those currents the field favors the ones whose own small magnet lines up with it, since a magnet along a field has the lower energy (Chapter 8, Box 8.1). So the current mixed in runs the opposite way to the shielding current, and its field adds to the applied field at the nucleus. Norman Ramsey worked out both parts for nuclei in molecules in 1950, the shielding part like Lamb's and a second, *deshielding* part from that mixing (Ramsey, 1950). For the hydrogen molecule the shielding constant is 2.68×10^{-5}, of which the deshielding part is -0.56×10^{-5} (Ramsey, 1950). For hydrogen, whose electron in a bond is in an s state, with no orbital angular momentum and its p states far above, the electrons change the field the nucleus meets mostly by shielding it. For most other nuclei, such as carbon, nitrogen, oxygen and fluorine, whose bonds hold p electrons near the nucleus, the deshielding part sets most of the differences

from one chemical setting to another (standard accounts of NMR). So the general statement is that the electrons change the field the nucleus meets, by an amount set by their states, mostly by shielding it.

That change is the *chemical shift*: the move of a nucleus's resonance away from the resonance of the bare nucleus, set by the states of the electrons round it, and so by the bonds it is part of. It is written in parts per million of the resonance frequency, measured from the resonance of a chosen reference molecule, and since the shielding is in proportion to the field, the shift in parts per million is the same in every magnet. The protons of the molecules of organic chemistry fall within about ten parts per million of one another, and carbon-13 within about two hundred (standard accounts of NMR). In 1951 James Arnold, Shrikrishna Dharmatti and Martin Packard found that the protons of ethanol give three lines, from the three hydrogens bound to its end carbon, the two bound to its middle carbon and the one bound to its oxygen, with areas in the ratio 3 to 2 to 1 (Arnold, Dharmatti and Packard, 1951). One kind of nucleus answered at three frequencies according to its place in the molecule.

Nuclei also feel one another, through the electrons of the bonds between them. A proton's spin, pointing with the field or against it, slightly changes the electrons of its bond, and they in turn change the field at a neighboring proton. So each line is split into a few lines, by an amount, a few hertz to a few hundred, that does not depend on the magnet's field: the *spin-spin coupling*, also called J coupling (standard accounts of NMR). A group of protons next to n equivalent protons is split into n + 1 lines, since the number of those n neighbors whose spins point with the field can be any whole number from 0 to n, which is n + 1 values. So in ethanol the line of the three end hydrogens is split in three by the two middle ones, and the line of the two middle hydrogens in four by the three end ones. The shifts tell a chemist what kinds of place a molecule's nuclei sit in, and the splittings tell which places are bonded next to which, and from both a molecule's structure can be read.

So we now know why the resonance reports the chemical surroundings. A field drives the electrons round the nucleus into currents whose field opposes it there, by Lenz's law, and in a molecule a second, deshielding part adds to the field. The nucleus meets a field changed, mostly lessened, by an amount set by its electrons' states, so the frequency of its resonance shifts by parts per million according to its bonds. And the nuclei's spins split one another's lines through the electrons of the bonds between them.

IX. Silent Nuclei

A sugar molecule holds six carbon atoms, six oxygen atoms and twelve hydrogen atoms, and nearly all of its mass is in the carbon and the oxygen. Yet its resonance spectrum shows only its hydrogens, unless a chemist looks for a faint signal from the rare carbon-13. Why are the carbon and oxygen that make most of living matter invisible to NMR?

They are silent because they are paired. Carbon-12, six protons and six neutrons, and oxygen-16, eight and eight, have every nucleon paired with one of its own kind, so they have spin zero (Section VI). A nucleus of spin zero has one orientation only, so there is no difference of energy between orientations for a photon to match, and it has no magnetic moment for a field to act on: it takes up nothing at any frequency, in any field. Nuclei with every nucleon paired are silent.

The silence is a help as much as a lack. The hydrogens of a molecule, and the 1.1 percent of its carbon atoms that are carbon-13 (Table 12.1), give a spectrum uncrowded by the rest of the molecule. A chemist dissolves a sample for proton NMR in a liquid whose hydrogen is deuterium, such as heavy water or a deuterated chloroform. Deuterium, of spin 1, answers at 6.54 megahertz in each tesla instead of 42.58, so it stays out of the proton spectrum, while ordinary hydrogen in the solvent, far more plentiful than the sample's, would drown the sample's signal (standard accounts of NMR; Table 12.1). And a biochemist who wants a protein's car-

bon and nitrogen to speak grows the protein on food made with carbon-13 and nitrogen-15, each of spin 1/2, in place of carbon-12 and nitrogen-14.

So we now know why carbon-12 and oxygen-16 are silent. Their nucleons are all paired, so their spin is zero, and a nucleus of spin zero has no second orientation to pass to and no moment for a field to act on. The silence follows from pairing alone, and it leaves the hydrogens of a molecule to speak for it.

X. A Gamma Ray and Its Recoil

A rifle kicks back against the shoulder of whoever fires it. The bullet carries momentum forward, so the rifle must carry as much backward, and the kick takes a share of the energy of the powder that would otherwise have gone into the bullet. A nucleus that gives off a gamma ray kicks back the same way. A sodium atom takes up the yellow light another sodium atom gives off, which is why a sodium lamp's light lights up sodium vapor. Can a nucleus take up the gamma ray of another nucleus of its own kind?

A nucleus left in a state above its lowest falls to a lower state by giving off a *gamma ray*, light of very high energy (Volume One, Chapter 5, Sections II and X). Iron-57, made when cobalt-57 captures an electron, is left in a state 14.4 keV above its lowest, a keV being a thousand electron volts, and it falls from that state by giving off a gamma ray of 14.4 keV (standard tables of nuclides). A state that lasts on average a time τ, read "tau", has its energy defined to within about $\hbar/\tau$, its *natural width*. So it is with a particle that decays: its mass is defined to within its width Γ, read "capital gamma", and its mean life is $\hbar/\Gamma$ (Volume One, Chapter 2, Section II). The 14.4 keV state of iron-57 lasts about 141 nanoseconds on average, so its natural width is 4.7×10^{-9} eV (computed; standard tables of nuclides): about one part in three trillion of its energy. In Box 12.2 I find what the kick takes.

Box 12.2. The recoil of a free nucleus

Premises. (1) Momentum is kept in every change (standard physics). (2) A photon of energy E carries momentum E/c (standard electromagnetism). (3) A nucleus of mass M moving with momentum p, slowly against c, has the energy of motion $p^2/(2M)$ (standard mechanics). (4) Energy is kept: the energy E_0 by which the excited state lies above the lower one goes into the gamma ray and the nucleus's motion together. (5) For iron-57: E_0 = 14,412.5 eV; Mc^2 = 56.935 atomic mass units times 931.494 MeV = 53,035 MeV (standard tables of nuclides; CODATA 2022 for the atomic mass unit).

Steps. By (1) and (2), a free nucleus at rest that gives off a gamma ray of energy E moves off with momentum E/c, opposite to the gamma ray. By (3), its energy of motion is $E_R = (E/c)^2/(2M) = E^2/(2Mc^2)$, the *recoil energy*. By (4), the gamma ray carries $E_0 - E_R$, to first order in the small ratio E_0/Mc^2. An identical nucleus at rest that takes up a gamma ray must also move off with the gamma ray's momentum, so it needs $E_0 + E_R$: the gamma ray of the first falls short of what the second needs by $2E_R$. By (5), for iron-57, $E_R = (14{,}412.5\text{ eV})^2/(2 \times 5.3035 \times 10^{10}\text{ eV}) = 1.96 \times 10^{-3}$ eV, and $2E_R$ is 3.9×10^{-3} eV.

Result. A free nucleus that gives off a gamma ray recoils, so the gamma ray carries less than the fall by $E^2/(2Mc^2)$, and an identical nucleus at rest needs more than the fall by the same amount. A nucleus at rest can take up another's gamma ray only if $2E_R$ is smaller than the natural width; for iron-57, $2E_R$ is about 840,000 times the width of 4.7×10^{-9} eV (computed), so free nuclei of iron-57 at rest do not take up one another's gamma rays.

The recoil grows as the square of the energy of the light, and that is why atoms and nuclei differ. Sodium's yellow light carries 2.10 eV, and its recoil, with sodium's mass, is 1.0×10^{-10} eV (computed). The upper state

of that light lasts 16.25 nanoseconds on average (Volz et al., 1996), so the natural width of the line is 4.1×10^{-8} eV (computed). The recoil is far inside the width, and free sodium atoms take up their own light freely. Iron-57's gamma ray carries about 6,900 times the energy of sodium's light, and its recoil, though its nucleus is the heavier, is about nineteen million times larger (computed), far outside its natural width.

Nuclei at a temperature move, and their motion adds to the account of Box 12.2, which was made for nuclei at rest. In a gas or a solid at a temperature, each nucleus moves. A gamma ray given off by a nucleus moving toward an absorber arrives with its frequency raised by the motion, the Doppler shift, by the share v/c for a speed v along the line. At room temperature the nuclei's motions shift the gamma rays of iron-57 by amounts ranging over about 2×10^{-2} eV, about six times $2E_R$ (computed from equipartition, Section V). That range is measured as the width at half height: the width of the range of shifts at the height where the number of gamma rays falls to half its greatest value. So the motion can make up the recoil's shortfall for some pairs of nuclei, and some gamma rays are taken up. Philip Moon did it on purpose in 1951, spinning a source of mercury-198's gamma rays on the tip of a fast rotor so that its motion toward the absorber made up the recoil (Moon, 1951). But the motion that restores some taking up also smears the line over a range about five million times its natural width (computed), and the sharpness that the natural width allows is lost.

So we now know why a free nucleus cannot take up the gamma ray of another of its kind. Momentum is kept, so a free nucleus recoils when it gives off a gamma ray, which then carries less than the fall by $E^2/(2Mc^2)$, while an identical nucleus at rest needs more than the fall by the same amount. For gamma rays the mismatch is far larger than the natural width, so nuclei at rest cannot take them up, and the thermal motion that can make up the mismatch destroys the line's sharpness.

XI. Emission Without Recoil

A skater who throws a heavy ball rolls backward. A thrower standing on solid ground throws the same ball and does not move: the kick goes through the thrower's feet into the ground, and the whole Earth takes it, so little that nothing can be seen. A nucleus fixed in a crystal stands on solid ground of a kind. Can the crystal take the recoil, and with it give the gamma ray back its full energy?

Rudolf Mössbauer found in 1958 that it can. Working with iridium-191 in a crystal cooled far below room temperature, he found that a share of the gamma rays was given off and taken up with no recoil lost, at the full energy of the fall and with the natural width (Mössbauer, 1958). He received the Nobel Prize in Physics for 1961 (standard accounts of the Mössbauer effect). The reason lies in Chapter 5's finding that a crystal's vibrations come in quanta. Box 12.3 contains the argument.

Box 12.3. Recoil-free emission

Premises. (1) A nucleus in a crystal is held at its place by its neighbors, and the crystal's vibrations take energy only in whole quanta, the phonons (Chapter 5, Section IV). (2) The gamma ray's momentum E/c must be taken up by something, since momentum is kept (Box 12.2). (3) A body of mass M_c, read "M c", that takes up the momentum E/c as a whole moves off with the energy $E^2/(2M_c c^2)$ (Box 12.2, with M_c in place of M). (4) For iron-57 the free recoil is $E_R = 1.96 \times 10^{-3}$ eV (Box 12.2); a gram of iron-57 holds 1.06×10^{22} atoms (computed from its mass of 56.935 atomic mass units). (5) The quanta of a crystal's vibrations reach up to about kΘ, with Θ the crystal's Debye temperature, the temperature at which kΘ equals the quantum of a crystal's highest mode (Chapter 5, Box 5.3); for iron Θ is about 470 kelvin, so kΘ is about 0.04 eV (Kittel, 1996).

Steps. The free recoil, 2×10^{-3} eV, is smaller than most of the crystal's quanta, about 0.04 eV, so by (1) the nucleus cannot hand its recoil energy to the lattice in a small amount: the lattice either takes a whole phonon or takes none. When a phonon is made, the gamma ray loses at least that phonon's energy, and it is not taken up by a nucleus at rest. When no phonon is made, the lattice's motions are unchanged, so by (2) the momentum is taken by the crystal as a whole, the nucleus moving only as part of the whole crystal. By (3), the energy then lost is $E^2/(2M_c c^2)$, smaller than the free nucleus's recoil by the ratio M/M_c of the nucleus's mass to the crystal's. By (4), for a crystal of one gram that ratio is $1/(1.06 \times 10^{22})$, about 10^{-22}, and the energy lost is about 2×10^{-25} eV, about 2.5×10^{16} times smaller than the natural width (computed).

Result. In a crystal, a share of the gamma rays is given off with no phonon made; for those the recoil is taken by the whole crystal, and the energy lost is smaller than a free nucleus's recoil by the ratio of the nucleus's mass to the crystal's, which for a crystal of any size that can be held is exceedingly small. Those gamma rays carry the full energy of the fall, with the natural width, and an identical nucleus held in a crystal can take them up in the same way.

This giving off and taking up of gamma rays with no energy lost to recoil is the *Mössbauer effect*. The share of gamma rays given off with no phonon made, the *recoil-free fraction*, is set by how far the nucleus moves about its place, and so by the temperature and the crystal's vibrations. It is $e^{-E^2\langle x^2\rangle/(\hbar c)^2}$, where $\langle x^2\rangle$ is the mean square distance the nucleus moves from its place along the gamma ray's direction, from its zero-point motion and its thermal motion together (Lamb, 1939; standard accounts of the Mössbauer effect). A nucleus held tightly, which moves little, gives most of its gamma rays without recoil. A gamma ray of low energy, whose momentum is small, is given off without recoil more often too. With Debye's account of the crystal's vibrations (Chapter 5, Box 5.3), the share for iron-57 in iron, with Θ about 470 kelvin, comes to about 0.93 at the lowest temperature and about 0.82 at room temperature (computed). So most of

iron-57's gamma rays are recoil-free even when warm, which is why iron-57 is the nucleus most used. Its share falls toward zero as the crystal is heated, since the thermal motion grows. Chapter 2's counting of the ways the crystal holds its energy sets the share at each temperature.

The recoil-free line is so sharp that the chemistry round the nucleus shows in it. A source of cobalt-57 in a metal gives off iron-57's gamma rays, and an absorber holding iron-57 in some chemical form takes them up. Moving the source toward or away from the absorber at a few millimeters a second shifts the gamma ray's energy by the Doppler shift, 48 nanoelectronvolts for each millimeter a second, about ten natural widths (computed). The absorption is measured against the speed (standard accounts of Mössbauer spectroscopy). Three things show in such a spectrum. The first thing that shows in such a spectrum is the line's place. The nucleus of iron-57 has a slightly different radius in its upper state than in its lower one, so the energy of the fall depends on the density of the s electrons at the nucleus, as the field shift of Section III does. That density differs between the iron of the source and the iron of the absorber, so the line's place moves: the *isomer shift*, the name physicists give to this move of a nucleus's line with the density of the electrons at the nucleus. It tells iron's oxidation states apart, the charges an atom would carry if the shared electrons of each of its bonds were given wholly to the atom of the pair that pulls them harder (Chapter 3, Section VII; standard accounts of Mössbauer spectroscopy). The line splits in two where the electrons' electric field changes from place to place across the nucleus, since the upper state of iron-57, of spin 3/2, has an electric quadrupole moment (Section VI): the *quadrupole splitting*. It tells the shape of the electrons' arrangement round the iron. And the line splits in six where the iron sits in a magnetic field, as in a magnet, since the field splits both states into their orientations (Section VII): the *magnetic hyperfine splitting*. The lower state, of spin 1/2, has two orientations, and the upper, of spin 3/2, has four, so there are eight pairs of an upper and a lower orientation. The gamma ray carries one unit ħ of angular momentum, so it can change the angular momentum along the field by one unit at most (Box 12.1, premise 4). Two of

the eight pairs differ by two units, and those two give no line, which leaves six. Small spectrometers of this kind rode on two of the rovers sent to Mars and read the iron minerals of its rocks (standard accounts of Mössbauer spectroscopy).

So we now know how a crystal gives a gamma ray its full energy. A crystal's vibrations come in quanta, so the recoil is either a whole phonon or nothing. When it is nothing, the whole crystal takes the momentum, and the energy lost is smaller than the free recoil by the ratio of the nucleus's mass to the crystal's, so the gamma ray is given off and taken up exactly, with its natural width. The share of such gamma rays is set by the temperature and the crystal's vibrations, and the line is sharp enough to read the electrons round the nucleus.

XII. Reading Gravitation in a Gamma Ray

A ball thrown straight up slows as it climbs, giving up energy of motion to the height it gains. Light thrown straight up cannot slow, but it can give up energy all the same, by arriving at a lower frequency than it left with. The difference over the height of a building is a few parts in a million billion. Can anything measure a frequency that finely?

Gravitation shifts frequencies. *The Gravitational Passage*, Chapter 16, Section III, names "the gravitational redshift" among the well-known features of the field of gravitation outside a mass, which its equations give. Light climbing out of a body's pull arrives at a lower frequency, and light falling into it at a higher one. The name redshift comes from visible light, whose color moves toward the red as its frequency falls. Near the Earth's surface, light climbing a height h has its frequency lowered by the share gh/c^2, with g the acceleration of a falling body, 9.81 meters a second in each second (standard physics, the form of the shift where the pull is as gentle as the Earth's). Over 22.5 meters that share is 2.46×10^{-15} (computed).

The recoil-free line of iron-57 can read it. For the 14.4 keV gamma ray the shift over 22.5 meters is 3.5×10^{-11} eV, less than a hundredth of the natural width, and it is the same as the Doppler shift of a source moving at 0.74 micrometers a second (computed). A line so sharp that its whole width is a hundred times that shift can have its center found to a small part of the shift by counting many gamma rays. Robert Pound and Glen Rebka sent the gamma rays of a source of cobalt-57 down and up through a height of 22.5 meters in a tower at Harvard in 1959, moving the source slowly to scan the line. They read a shift of $(2.56 \pm 0.25) \times 10^{-15}$, lowered going up and raised going down, the shift gh/c^2 that gravitation makes, and published it in 1960 (Pound and Rebka, 1960; standard accounts of the Pound-Rebka experiment). Robert Pound and Joseph Snider later read the same shift more finely, to about one percent of its size (Pound and Snider, 1964).

Pound and Rebka had to master a second shift. A nucleus vibrating in its crystal moves back and forth too fast for its Doppler shifts of Section X, the shares v/c toward and away, to do anything but cancel in the line's center. But relativity shows that a moving clock runs slow: at a speed v, small against c, its rate falls by the share $v^2/2c^2$ (standard physics, the special theory of relativity). Every nucleus is a clock, its gamma ray the count of its ticks, so the vibration lowers the gamma ray's frequency by the share $\langle v^2 \rangle / 2c^2$, with $\langle v^2 \rangle$ the mean of the square of the nucleus's speed. That share depends on the square of the speed, so it does not cancel between toward and away, and it grows with the temperature: the *second-order Doppler shift*. For iron-57 it changes the line by 2.4×10^{-15} for each kelvin of difference in temperature between source and absorber (computed from equipartition), as much as the whole effect of gravitation over the tower. So Pound and Rebka measured the temperatures of both and corrected for the difference (standard accounts of the Pound-Rebka experiment). The recoil-free event is free of the first-order Doppler shift's smearing, since the nucleus moves only with the whole crystal, and that is what keeps the line at its natural width.

So we now know how a gamma ray reads gravitation. The recoil-free line of iron-57 is so sharp that the share 2.46×10^{-15} by which gravitation shifts a frequency over 22.5 meters of height can be read in it, once the second-order Doppler shift, which grows with the crystal's temperature, is corrected for at both ends. Pound and Rebka read it.

XIII. Decays the Atom Does Not Touch

A bank keeps its gold in a vault deep inside the building, under the lobby, behind walls a meter thick. The crowds in the lobby, the traffic in the street and the weather outside never reach it. A nucleus that decays sits at the center of its atom, and its electrons, its chemistry and its surroundings lie all around it. Does what happens to the atom change how fast its nucleus decays?

For most decays it scarcely does, and the reason is where the nucleus sits. An alpha decay, a beta decay, a gamma ray, a fission: each is set by the strong force and the weak interaction acting within the nucleus, over distances of a few femtometers. Each sets free an energy of thousands to millions of electron volts (Volume One, Chapter 5). The electrons are far away, and the energies they deal in are far smaller. How far away they are follows from the order of two masses, the electron's against the pion's, and from the smallness of α, the strength of electromagnetism.

The nucleus is about as large as the reach of the force between nucleons, since a nucleon holds only its neighbors (Volume One, Chapter 4, Section VI). That force is carried by mesons, which have mass, so it reaches about the pion's *own length*, $\hbar/(mc)$, the length that a particle's mass, $\hbar$ and c make together, 1.41 fm for the pion (Volume One, Chapter 1, Section III, and Chapter 4, Section IV). A nucleus of A nucleons has a radius of about 1.2 $A^{1/3}$ fm (Volume One, Chapter 4, Section VI). The atom's size is the Bohr radius, which is the electron's own length divided by α: $a_0 = \hbar/(m_e c\alpha)$ (Volume One, Chapter 7, Section V). The electron is 273 times lighter than the pion, so the electron's own length, 386 fm, is

already far larger than the reach of the force that sets the nucleus's size (Volume One, Chapter 7, Section V, for the 386 fm). The further factor $1/\alpha = 137$ then makes the atom larger still. The ordering of the electron's and the pion's masses and the smallness of α together put the nucleus far inside its atom. The Bohr radius, 52,918 fm, is 44,000 times a radius of 1.2 fm, 11,500 times the radius of iron-56 and 7,100 times the radius of uranium-238 (computed). Even the innermost electron of uranium, held 92 times closer than hydrogen's, is held at about 575 fm, some 77 times the nucleus's radius (computed, from its size a_0/Z, Volume One, Chapter 9, Section II).

So the electrons spend almost none of their time inside the nucleus. An S electron is found at the center with the weight $|\psi(0)|^2 = Z^3/(\pi a_0{}^3)$ for the innermost state (Volume One, Chapter 8, Box 8.2, with the charge Z). So the share of its time inside a nucleus of radius R is about $(4/3)(ZR/a_0)^3$, the weight at the center times the nucleus's volume. That share is about 5 parts in 10^{15} for the electron of hydrogen inside the proton, 1.5 parts in 10^8 for the innermost electrons of iron, and at least 3 parts in a million for those of uranium, whose innermost electrons relativity draws closer still (computed). And the energies differ as much: a chemical bond changes the electrons' energy by a few electron volts, against the thousands to millions of electron volts a nuclear decay sets free.

So the half-lives of alpha and beta emitters are found unchanged by heat, pressure and chemical form to the precision with which the half-lives are measured, apart from the few decays of Section XIV (Emery, 1972). In Volume One, Chapter 5, In Use, we built methods of dating on it: carbon-14 dates what once lived, potassium-40 and its argon date rock, and the two decays of uranium to lead date the oldest rock. Each works because a nucleus's chance of decaying in each second is set inside the nucleus and not by the rock or the bone around it. Radiometric dating rests on the nucleus lying far inside its atom.

So we now know why most decays are untouched by the atom. They are set by the strong force and the weak interaction within the nucleus, at energies of thousands to millions of electron volts. The nucleus lies far inside its atom because the electron is far lighter than the mesons that set the nucleus's size and α is small. The electrons spend almost none of their time there, and chemistry changes their energy by only a few electron volts.

XIV. Decays That Depend on the Electrons

The vault of Section XIII has one door, and a few of the bank's dealings pass through it: a clerk carries something in, or something out. Those dealings depend on who is in the lobby. Some decays of a nucleus take one of its own atom's electrons in, or send their energy out through one, or place a new electron in the atom. Do those decays depend on the atom around the nucleus?

They do, and the rule is one: a decay that takes in, gives to or places an electron of the atom depends on that electron's state, and so on the atom and its chemistry. *The Branches of the Kinds*, Chapter 2, Section IV, states the three cases of the weak interaction: "The rate of electron capture (a nucleus taking up one of its atom's electrons) is set by the electron density at the nucleus, which changes slightly with the chemical form of the atom. A fully ionized atom has no electron to capture, so it cannot decay by electron capture. A decay too weak to send its electron into free space can still proceed in a fully ionized atom by placing the electron in an empty bound state (bound-state beta decay), so an atom that is stable when whole can decay when stripped". In this section we follow each, and add a fourth, through the electromagnetic force.

The first of the three cases is *electron capture*, in which the nucleus takes in one of its own atom's electrons and gives off a neutrino, $p + e^- \rightarrow n + \nu_e$ within the nucleus (Volume One, Chapter 5, Section II). It is the same change through the weak interaction as positron emission, in which a pro-

ton becomes a neutron by giving off a positron, the electron's antiparticle, and a neutrino, read with the electron taken in instead of the positron given off. A particle given off and its antiparticle taken in change a system's charge and its lepton number alike, and the laws of a change allow the one in place of the other, the rule physicists call crossing (standard physics). So wherever a proton in a nucleus can become a neutron, it can do so by either route, and charge is kept by both: the proton's charge leaves with the positron, or is canceled by the electron's. Capture needs no energy for a positron to be made, so it is open wherever the parent atom is heavier than the daughter atom at all. Positron emission is open only where the parent atom is heavier by more than 1.022 MeV, twice the electron's rest energy of 0.511 MeV, since the decay must make a positron and the daughter is left with one electron more than its new nuclear charge, an electron the atom sheds (Volume One, Chapter 5, Section II). Beryllium-7 lies only 0.862 MeV above lithium-7, so it can decay only by capture (Volume One, Chapter 5, Table 5.1).

The capture takes an electron from where it is at the nucleus, so its rate goes as the weight of the electrons' states at the center of the atom, the S states, which alone reach the center (Section III). The chemical form of the atom changes that weight slightly, most for a small atom whose few electrons are all near the nucleus, and beryllium-7 is the plain case. Takeshi Ohtsuki and his colleagues held beryllium-7 inside the cage of a carbon molecule of sixty atoms and found its half-life to be 52.68 $\pm$ 0.05 days, against 53.12 $\pm$ 0.05 days in beryllium metal, a difference of 0.83 percent (Ohtsuki et al., 2004). The *half-life* is the time in which half of a collection of radioactive nuclei decays (Volume One, Chapter 5, Section I).

The second case is the stripped atom. Take every electron from an atom of beryllium-7, and it has no electron to capture, and no other decay is open to it: a bare beryllium-7 nucleus lasts. The decay that the neutral atom makes with a half-life of 53 days depends wholly on its electrons.

The third case is *bound-state beta decay*, the reverse case. A beta decay that turns a neutron into a proton makes an electron, and in a neutral atom that electron must leave for free space, since the atom's lowest states

are full. In a stripped atom the lowest states are empty, so the new electron can be placed in one of them, and it then keeps the binding of that state instead of paying the energy to leave. For a heavy nucleus that binding is large. The innermost state of a single electron round a nucleus of charge Z is bound by about Z^2 times the Rydberg energy, 13.6 eV, the binding of hydrogen's electron with the proton held fixed (Volume One, Chapter 9, Section II). For holmium, Z = 67, that is about 60 keV, before the corrections of relativity (computed). Dysprosium-163 cannot beta decay as a neutral atom, since holmium-163, its daughter, is the heavier atom, by 2.83 keV (Eliseev et al., 2015). Stripped of all 66 of its electrons in a storage ring, where bare ions circle for weeks, dysprosium-163 decays to holmium-163, its new electron placed in an empty inner state, with a half-life of 47 ± 5 days (Jung et al., 1992). An atom that lasts when whole decays when stripped. Rhenium-187, which as a neutral atom beta decays with a half-life of about 41 billion years, decays when fully stripped with a half-life of 32.9 years (Bosch et al., 1996).

The fourth case goes through the electromagnetic force. A nucleus in an excited state can give its energy to one of its atom's electrons, which then flies out in place of a gamma ray: *internal conversion* (Volume One, Chapter 5, Section X). It too takes place where the electron's state reaches the nucleus, so its share of the decays changes with the chemical form. Technetium-99m is an isomer, a long-lived excited state of a nucleus (Volume One, Chapter 5, Section X). Kenneth Bainbridge, Maurice Goldhaber and Elizabeth Wilson found in 1953 that it decays at rates that differ by 0.27 percent in potassium pertechnetate and in technetium sulfide (Bainbridge, Goldhaber and Wilson, 1953). And internal conversion stops in a fully stripped atom, which has no electron to give the energy to, leaving the gamma ray as the only way down (standard accounts of internal conversion).

So we now know which decays depend on the atom and why. A decay that takes in an electron (capture), places one in the atom (bound-state beta decay), or gives its energy to one (internal conversion) depends on how much of that electron's state reaches the nucleus, which the chemical

form changes by up to about a percent. Capture is the change through the weak interaction that positron emission makes, read with the electron taken in. Strip the atom, and capture and conversion cannot happen at all, while bound-state beta decay can start, so that an atom stable when whole decays when stripped.

XV. The Clock from Indistinguishable Atoms

Two pendulum clocks built side by side by one clockmaker, from one drawing, with rods cut from one bar of brass, drift apart within weeks. Their rods are not quite the same length, their pivots not quite the same, and a warm room lengthens one rod more than the other. No two things made by hands are the same thing. Is there a clock that no two copies of could ever disagree?

Every atom carries one, and the nucleus winds it. In Volume One, Chapter 8, Section VII, we found that the proton is a magnet too, and that the electron's and the proton's magnets meet, so hydrogen's lowest level splits in two, by whether the two spins add or oppose. That splitting is the *hyperfine structure*, and in hydrogen it is 1420.405751768 megahertz, the frequency of the 21 cm line (Hellwig et al., 1970). Every atom whose nucleus has spin has such a splitting. In an S state, which reaches the nucleus, the splitting comes from the electron's magnet found at the nucleus itself, in proportion to the weight of its state there (Fermi, 1930). This part is called the *Fermi contact interaction*, and it is why the splitting of an atom's lowest level, an S state in hydrogen and in the alkali metals, is large and simple. Cesium-133, the only cesium that lasts, has a nucleus of spin 7/2 and one outer electron in an S state, and its lowest level splits in two, at 9,192,631,770 hertz (International Bureau of Weights and Measures, the definition of the second). Box 12.4 shows why such a frequency is a standard.

Box 12.4. The clock from indistinguishable atoms

Premises. (1) The principle of identity: "what no comparison can distinguish, in any way at all, even in principle, is one thing and not two" (*The Quantum Passage*, Chapter 8, Section VI; Chapter 1, Section IV). (2) Particles of one kind are alike in every way that any measurement can register: every electron in the universe is the same kind of thing as every other, with the same mass, the same charge and the same behavior, wherever and whenever it is found, and so is every proton and every neutron (Volume One, Chapter 1, Section II). (3) An atom of one kind, a nucleus of one charge and one number of neutrons with its electrons in their lowest state, is built of the same parts, held by the same forces, with the same values of $\hbar$, c, α and the masses, wherever it is found (Volume One, Chapter 7, Section XI). (4) The frequency of the light that matches the difference of two of an atom's levels is set by what the atom is: its parts, the forces between them and the values of (3) (Volume One, Chapter 7, Section VII; Section VII of this chapter for a splitting by a field). (5) A clock is a count of the cycles of a regular process, and a standard is a thing that is the same wherever it is found (Volume One, Chapter 7, Section XI, "a comparison of a thing with a standard that is the same wherever the standard is found").

Steps. By (2) and (3), two atoms of one kind, each left to itself in its lowest state, are alike in every way a measurement can register, apart from where each one is. By (1), what the one atom is and what the other is are then one thing and not two: they are atoms of one kind at two places, distinguished only by where they are (Chapter 5), and no comparison finds any property in which they differ. By (4), the frequency of a transition between two of their levels is a property set by what the atom is, so it is the same for both, and for every atom of that kind, everywhere in the universe and at every time. By (5), counting the cycles of light at that frequency is a clock whose standard is the same wherever an atom of that kind is found.

Result. Atoms of one kind cannot be told apart, so the frequency of any transition of theirs is the same for every such atom everywhere in the universe: it is a standard of frequency, and so of time. The argument holds for every transition of every kind of atom, the hyperfine splitting and every optical line alike; which transition is chosen as the standard is a choice of practice, made by how finely its frequency can be read.

What makes two clocks built from atoms disagree is what is around the atoms, never the atoms themselves. It is a stray magnetic field, collisions with other atoms, the atoms' own motion, which shifts the frequency by the Doppler shift, and the height at which the clock stands, since gravitation shifts frequencies (Section XII). The definition of the second therefore names the atom left alone: "The second, symbol s, is the SI unit of time. It is defined by taking the fixed numerical value of the caesium frequency $\Delta\nu_{Cs}$, the unperturbed ground-state hyperfine transition frequency of the caesium-133 atom, to be 9 192 631 770 when expressed in the unit Hz, which is equal to s^{-1}" (International Bureau of Weights and Measures, the definition of the second). SI is the International System of Units, the international units of the earlier chapters, and Hz is the hertz, one cycle each second. *Measurement*, Chapter 2, Section IV, states the same definition as a matter of method: "The second is defined by the number of cycles, 9 192 631 770, of the radiation that caesium atoms absorb in a stated transition". Louis Essen and Jack Parry built the first cesium clock at the National Physical Laboratory, near London, in 1955, and the second has been defined by cesium since 1967 (standard accounts of atomic clocks). The best cesium clocks, in which a ball of slow, cold cesium atoms is tossed upward through a microwave cavity and falls back through it, now keep the frequency to about one part in 10^{16} (standard accounts of atomic clocks).

Box 12.4 holds for every transition of every kind of atom, so cesium is the present choice of standard and not the only possible one. Light gives a finer clock than microwaves, because it swings far more often in each second, so each second is divided more finely. The light that drives the

clock transition of strontium swings about 429 trillion times a second (429,228,004,229,873 hertz, the frequency the International Bureau of Weights and Measures recommends for it; standard accounts of atomic clocks), some 46,700 times as often as cesium's microwaves (computed). Clocks built on such transitions of visible light, in strontium atoms held in a lattice of laser light and in single ions of ytterbium, now surpass cesium's. In a clock of strontium atoms in Boulder, Colorado, every shift that the atoms' surroundings make in the frequency, from stray fields, collisions and the heat of the room, has been measured and taken out to within 8.1 parts in 10^{19} (Aeppli et al., 2024). That figure is the measure of how closely the clock ticks at the frequency of the atom left alone, the frequency a standard names. Such clocks have read the shift that gravitation makes across a single millimeter of height within one small cloud of atoms, about one part in 10^{19} (Bothwell et al., 2022; computed from gh/c^2). The International Bureau of Weights and Measures is preparing to redefine the second on an optical transition, possibly in 2030 (International Bureau of Weights and Measures, the redefinition of the second). Whichever atom is chosen, the reason it can be a standard is the reason of Box 12.4.

Hydrogen's own splitting keeps time too. In Volume One, Chapter 8, In Use, we found it at work. Hydrogen masers, amplifiers of microwaves by atoms passing together from an upper level to a lower one, keep radio telescopes thousands of kilometers apart in step, and the satellites of the European navigation system Galileo carry them. And the 21 cm line of the hydrogen between the stars maps the galaxy's spiral arms.

So we now know why the atom makes a clock. The nucleus's magnet splits the atom's lowest level by the hyperfine structure, and atoms of one kind cannot be told apart, so the frequency of that splitting, or of any other transition of theirs, is the same for every such atom everywhere in the universe. Counted, it is a standard of time: cesium's splitting today, and a transition of light when the second is redefined.

In Use

The hospital scanner of Section I is nuclear magnetic resonance turned into pictures, magnetic resonance imaging, called MRI. Its superconducting magnet, most often of 1.5 tesla and often of 3 (Chapter 9, In Use), sets the body's hydrogen nuclei, in its water and its fat, to answer at 64 or 128 megahertz (Box 12.1). Paul Lauterbur showed in 1973 how to tell where each signal comes from. Add to the steady field a small field that grows along one direction, a gradient, and the resonance frequency grows along that direction too, so each frequency in the signal belongs to one slice of the body. Gradients along three directions in turn locate each signal in space. Lauterbur and Peter Mansfield shared the Nobel Prize in Physiology or Medicine for 2003 (standard accounts of MRI). The pictures' contrast comes from the two relaxation times of Section VII: the protons of fat and of water, and of healthy and injured tissue, return to the field and fall out of step at different rates. So a scan timed to stress one time or the other shows fat bright, or fluid bright. A contrast agent of gadolinium, an atom with seven unpaired electrons and so a strong magnet, shortens the times of the protons near it and marks where it has gone. And functional MRI follows the blood: hemoglobin that has given up its oxygen is a paramagnet and hemoglobin carrying oxygen is not, so the working parts of the brain, flooded with fresh blood, change their signal (standard accounts of MRI). About 50,000 MRI scanners are at work in the world (standard accounts of MRI).

In chemistry, NMR is the commonest way of finding a new molecule's structure. The chemical shifts of Section VIII say what kinds of place its hydrogens and its carbon-13 nuclei sit in, the spin-spin couplings say which places are bonded next to which, and spectra of two and more frequencies, Ernst's method of Section VII, say which nuclei lie near which in space. For the molecules of life, the same methods, with proteins grown on carbon-13 and nitrogen-15 (Section IX), give the shapes of proteins as

they move in water. In the search for medicines, a protein's NMR spectrum, watched as small molecules are added, shows which of them bind to it and where (standard accounts of NMR).

The kinetic isotope effect of Section IV is now a medicine's design. Many drugs are broken down in the liver by enzymes that pull a hydrogen atom off a carbon atom in their slowest step. With deuterium in that place, the bond is harder to break, the breakdown is slower, and the drug lasts longer in the body. Deutetrabenazine, tetrabenazine with deuterium at its points of attack, was approved in the United States in 2017 to treat the movements of Huntington's disease, and it lasts longer in the body than tetrabenazine. Deucravacitinib, approved in 2022 for psoriasis, was designed with deuterium from the start (standard accounts of deuterated drugs). Heavy water does other work. As the moderator of the Canadian reactors called CANDU, for Canada deuterium uranium, it slows the neutrons of fission while taking few of them in, so those reactors can burn natural uranium (standard accounts of heavy water). And it is the solvent of Section IX in which chemists dissolve their samples for proton NMR.

Isotopes also keep the record of climate. A water molecule that carries oxygen-18 in place of oxygen-16 is heavier, so it evaporates a little less readily and condenses a little more readily (Sections IV and V). As moist air moves toward the poles and cools, its heavy molecules rain out first, and the colder the air when its snow falls, the less oxygen-18 the snow holds. The ice of Greenland and Antarctica holds that snow layer by layer. The ratio of oxygen-18 to oxygen-16 in each layer, measured against a standard of ocean water in parts per thousand, follows the temperature of the past, over hundreds of thousands of years in the cores drilled at Vostok (standard accounts of oxygen-18 records). In the ocean, the shells of small animals called foraminifera take up oxygen-18 in a share that rises by 0.22 parts per thousand for each degree of cooling of the water (Epstein, Buchsbaum, Lowenstam and Urey, 1953). Their shells in the sediments of the sea floor record the waters' temperature and the volume of the ice on land over the last five million years (Lisiecki and Raymo, 2005).

The atomic clocks of Section XV run the world's time and its navigation. International Atomic Time is a weighted average of about 450 clocks in some 80 laboratories, and the time of every country is set from it (standard accounts of atomic clocks). Each satellite of the Global Positioning System carries cesium and rubidium clocks, and a receiver finds its place from the times at which the satellites' signals arrive. A nanosecond's error in a clock is 30 centimeters of error in place, since light travels that far in a nanosecond (computed). The satellites' clocks, higher in the Earth's pull and moving fast, run fast against clocks on the ground by about 38 microseconds a day: the gravitational shift of Section XII, less the slowing of moving clocks of the same section (Ashby, 2003). They are built to run slow by that amount, their frequency set to 10.22999999543 megahertz in place of 10.23, so that they keep time with the ground (Ashby, 2003; standard accounts of the Global Positioning System). Uncorrected, that shift would move the places found by about 11 kilometers in a day (computed: 38 microseconds times c).

Summary

The nucleus is almost hidden inside its atom, because it is heavy, so it nearly stays where it is, and small, so the electrons answer almost wholly to its charge. It shows through in five places. Isotopes, nuclei of one charge with different numbers of neutrons, give atoms whose electrons meet the same charge, so their states, shells and bonds are almost the same. They differ in four ways. The nucleus moves a little with the electrons, which shifts every level by about the electron's mass over the nucleus's, with a further part from the correlated motions of many electrons. The nucleus has a size, which lifts the S states that reach it by an amount set by its mean square radius. A held atom keeps a zero-point energy that goes as one over the square root of its mass. So a heavier isotope sits lower in its bond, holds it more strongly and reacts more slowly, up to about seven times for deuterium against hydrogen at room temperature and

more with tunneling. And whatever goes with the atom's motion differs, for a separate reason, equipartition. Heavier isotopes diffuse more slowly, by the square root of the mass ratio, carry heat differently, and in a metal whose electrons pair through the lattice pair them at a lower temperature, while a centrifuge separates isotopes by the difference of their masses.

Nucleons of one kind pair with opposite spins, so a nucleus with every nucleon paired has spin zero. One unpaired nucleon always gives a spin of one half or more, and one unpaired proton with one unpaired neutron usually gives a spin of one or more, though the two can cancel. A nucleus with spin is a magnet of a few nuclear magnetons, smaller than an electron's moment by about the ratio of the masses. In a field its orientations differ in energy in proportion to the field, since the energy of a moment in a field that the moment does not change is linear in the field. So it takes up radio waves at $f = \gamma B/2\pi$, 42.58 megahertz in each tesla for hydrogen (Box 12.1): nuclear magnetic resonance. The electrons, driven round by the field, change the field the nucleus meets, mostly by opposing it, by Lenz's law, with a deshielding part in molecules, so the frequency shifts by parts per million with the nucleus's chemical surroundings. And nuclei with every nucleon paired are silent.

A free nucleus that gives off a gamma ray recoils, since momentum is kept, so its gamma ray falls short of what an identical nucleus at rest needs by twice $E^2/(2Mc^2)$, far more than the natural width (Box 12.2). Thermal motion can make up the shortfall only by smearing the line. In a crystal, whose vibrations come in quanta, a share of the gamma rays is given off with no phonon made, the whole crystal takes the recoil, and the loss is smaller than the free nucleus's by the ratio of the nucleus's mass to the crystal's (Box 12.3). Those gamma rays are given and taken up exactly, sharp enough to read the chemistry round the nucleus and the shift that gravitation makes over 22.5 meters. Most decays are set inside the nucleus, which lies far inside its atom because the electron is far lighter than the mesons that set the nucleus's size and α is small. So heat, pressure and chemistry scarcely touch them, and radiometric dating rests on that. Electron capture, internal conversion and bound-state beta decay depend on

the electrons' states at the nucleus, so chemistry changes them by up to about a percent. Stripping an atom stops capture and conversion, and it can start a beta decay in an atom that lasts when whole. Atoms of one kind cannot be told apart, so the frequency of any of their transitions is the same for every such atom everywhere in the universe, a standard of time (Box 12.4). Cesium's hyperfine splitting defines the second, and clocks built on transitions of light now surpass it.

I rest this chapter on two results, because together the two results answer the reader's question, how an instrument sees a nucleus that chemistry ignores. The scanner reads some nuclei and not others because of how nucleons pair, and a crystal gives the nucleus's gamma rays their full sharpness because its vibrations come in quanta. The silence of nuclei with every nucleon paired follows from pairing alone: paired nucleons leave spin zero, and a nucleus of spin zero has no second orientation to pass to and no moment for a field to act on. The exact giving off and taking up of gamma rays in crystals follows from the crystal's vibrations coming in quanta: a recoil that is either a whole phonon or nothing is, when it is nothing, taken by the whole crystal. In both, the rung below shows through the rung above: the nucleus, hidden by its atom, is read through the atom's own electrons and the crystal's own vibrations.

Throughout, matter has been ordinary matter: atoms a few tenths of a nanometer apart, held off from one another by exclusion, which makes matter stiff, and pressed by nothing stronger than the air. In a star, gravity presses matter with the weight of a whole star. Exclusion makes matter stiff. What happens when gravity presses it hard enough?

✶

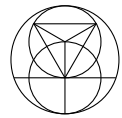
KEY CONCEPTS

- **Normal and specific mass shifts.** The shift of an atom's levels between isotopes because the nucleus moves a little with its electrons, by about the electron's mass over the nucleus's; and the further part from the correlated motions of many electrons.

- **Field shift; King plot.** The lifting of the S states by the nucleus's size, in proportion to its mean square radius, largest in heavy atoms; and the comparison of two lines' shifts across several isotopes that takes the mass and field parts apart.
- **Graham's law.** The leaking of a gas through fine pores at a rate in proportion to its molecules' speed, which at one temperature goes as one over the square root of the mass, by equipartition; the basis of separating isotopes by gaseous diffusion.
- **The rule for nuclear spin.** A nucleus's spin, its angular momentum in itself, is zero when every nucleon is paired, one half or more with one unpaired nucleon, and usually one or more with one unpaired proton and one unpaired neutron, which can cancel.
- **Gyromagnetic ratio; Larmor frequency.** The ratio γ of a nucleus's moment to its angular momentum; and $f = \gamma B/2\pi$, the frequency at which its moment swings round a field B and at which it takes up radio waves, 42.58 megahertz in each tesla for hydrogen.
- **Nuclear magnetic resonance (NMR).** The taking up of radio waves by nuclei with spin in a magnetic field, at the frequency that matches the difference of energy between neighboring orientations, which is in proportion to the field.
- **Longitudinal and transverse relaxation times.** T_1, the time in which tipped nuclear moments return to lie along the field; and T_2, the time in which they fall out of step; the basis of MRI's contrast.
- **Electron spin resonance.** The same taking up of photons by unpaired electrons, at 28.02 gigahertz in each tesla.
- **Lenz's law; shielding; deshielding.** A current driven by a changing field makes a field that opposes the change; so the electrons round a nucleus lessen the field it meets, by the shielding constant σ; and, in molecules, a second part of the opposite sign from the mixing of higher states.
- **Chemical shift.** The move of a nucleus's resonance, in parts per million, set by the states of the electrons round it, and so by its bonds.

- **Spin-spin coupling.** The splitting of one nucleus's line by the spins of nearby nuclei, through the electrons of the bonds between them, the same in every field.
- **Silent nuclei.** Nuclei with every nucleon paired, such as carbon-12 and oxygen-16, which have spin zero and take up nothing in a magnetic field.
- **Natural width; recoil energy.** The range $\hbar/\tau$ within which the energy of a state lasting a time τ is defined; and $E^2/(2Mc^2)$, the energy a free nucleus of mass M takes in recoil when it gives off a gamma ray of energy E.
- **Mössbauer effect; recoil-free fraction.** The giving off and taking up of gamma rays by nuclei held in a crystal with no energy lost to recoil, the whole crystal taking the momentum when no phonon is made; and the share of gamma rays so given off, $e^{-E^2\langle x^2\rangle/(\hbar c)^2}$, set by the temperature and the crystal's vibrations.
- **Isomer shift; quadrupole splitting; magnetic hyperfine splitting.** The three marks of chemistry and magnetism on a Mössbauer line: its move with the density of s electrons at the nucleus, its splitting in two by a changing electric field across the nucleus, and its splitting in six by a magnetic field.
- **Second-order Doppler shift.** The slowing of a vibrating nucleus's clock by relativity, growing with the temperature, which does not cancel in a line's center.
- **Crossing.** The rule that allows a particle given off in a change to be replaced by its antiparticle taken in; by it, electron capture is the change of positron emission with the atom's electron taken in instead of a positron given off.
- **Bound-state beta decay.** A beta decay that places its new electron in an empty bound state of a stripped atom, so that an atom stable when whole decays when stripped.

- **Fermi contact interaction.** The part of the hyperfine splitting that comes from an S electron's magnet found at the nucleus itself, in proportion to the weight of its state there.
- **Atomic clock.** A count of the cycles of light matching a transition of an atom; a standard because atoms of one kind cannot be told apart, so the frequency is the same for every such atom everywhere in the universe.



Chapter 13

Matter Pressed Together

CHAPTER OVERVIEW

A star that has burned its fuel can no longer hold itself up by the pressure of its heat. Yet some such stars, the white dwarfs, hold the mass of the Sun in a ball smaller than the Earth, and others, the neutron stars, hold more than the Sun's mass in a ball some twenty-five kilometers across. In this chapter I find what holds them up. The answer is exclusion. No two electrons share a state, so electrons crowded together fill their states from the lowest up to a top, the Fermi level, and squeezing them shortens their waves and raises the top. The crowd pushes back with a pressure that needs no heat at all, the degeneracy pressure, which falls as one over the particles' mass, so in a white dwarf it is the electrons that hold the star up (Box 13.1). A heavier white dwarf is smaller, and in the heaviest the electrons move near the speed of light, where their pressure grows more slowly with the squeezing. Then the electrons' pressure and the star's own gravity grow alike as the star shrinks, and above one mass no size holds: the Chandrasekhar mass, about 1.4 times the Sun's, made of $\hbar$, c, the constant of gravitation and the nucleon's mass alone (Box 13.2). Squeezed further, the electrons at the top of their sea, at the Fermi energy, carry more than the 0.782 MeV that keeps a hydrogen atom from becoming a neutron, and the electrons are pressed into the protons, which become neutrons. The neutrons then last, since the electrons their decay would make have no empty state to go to. A neutron star is matter at about the density of a nucleus, held up by the exclusion of its neutrons

> and by the push of the force between nucleons where they are pressed closer than they are in a nucleus. The heaviest yet weighed has 2.08 times the Sun's mass, in a radius about twice the radius that its horizon would have, the horizon being the bound from inside which nothing, not even light, can leave. Beyond what its matter's pressure holds, the account of a body belongs to gravitation, and *The Gravitational Passage* states it: bound structures end in black holes, bodies whose gravity lets nothing out. Neutron stars that spin and shine are pulsars, the steadiest clocks in the sky, and two that merge send out gravitational waves and make the heaviest elements.

I. A Star Smaller than the Earth

Chapter 12 ended with a question: exclusion makes matter stiff, so what happens when gravity presses it hard enough?

The brightest star in the night sky, Sirius, has a faint companion, so close to it that only a large telescope can pick it out of the glare. The two circle each other every 50.13 years, and from their motion the companion's mass can be weighed: 1.018 ± 0.011 times the mass of the Sun (Bond et al., 2017). Its light, climbing out of its pull, arrives with its frequency lowered by gravitation, as light climbing a tower does (Chapter 12, Section XII), but by far more. Near the Earth the share is gh/c^2 for a climb of height h. Light leaving a star climbs from the star's surface all the way out, through a pull that weakens as it climbs, and the whole climb adds up to the share $GM/(Rc^2)$ for a star of mass M and radius R, with G the constant of gravitation (standard physics). So from the shift and the mass the radius follows: about 5,600 kilometers (computed from Joyce et al., 2018), smaller than the Earth, whose radius is 6,371 kilometers. So Sirius B packs the mass of the Sun into less than the Earth's room. Its mean density is about 2.8 tonnes in each cubic centimeter (computed): a teaspoon of it would weigh about 14 tonnes.

An ordinary star such as the Sun holds itself up by its heat. Its gas is hot, its particles move fast, and the pressure of a hot gas grows with its temperature, pressure being the force for each unit of area with which a gas or a liquid presses on what holds it (Chapter 2, Section XIV). For a gas of n particles in each unit of volume the pressure is P = nkT (Chapter 4, Box 4.1). The fusion in its core keeps it hot (Volume One, Chapter 6, Section II). A star such as Sirius B has burned its fuel and has no fusion to keep it hot, and it has been cooling, by shining, for many millions of years. Heat cannot be what holds it up.

So the reader's question is this: what holds up a white dwarf and a neutron star?

A *white dwarf* is the cooling remnant of a star that has burned its fuel, about as massive as the Sun and about as large as the Earth, and Sirius B is one. A *neutron star*, as Volume One, Chapter 6, Section IV, defines it, is a body about as massive as the Sun, or more, packed to the density of a nucleus and made mostly of neutrons, the collapsed core of a massive star. I find that both are held up by the first rule of the kinds, exclusion, and that the second is held up by the force between nucleons as well. I find too that each has a mass above which nothing in it can hold.

II. Pressure Without Heat

In Volume One, Chapter 1, In Use, I pressed a hand on a table, and the hand stopped, though both are almost wholly empty space: the electrons of the hand cannot take the states that the table's electrons already hold. In Chapter 6, Section IV, I filled a theater from the front, one person to a seat, every seat taken up to some row. Now take away half the rows and keep the crowd: the people of the rows removed must sit further back, in dearer seats, and the crowd as a whole holds more. How can a crowd of electrons push back when it is squeezed, with no heat in it at all?

Electrons are fermions, a fermion being a particle whose spin is an odd number of halves (Chapter 1, Section IV). No two fermions of one kind share a state: the exclusion principle, which Volume One, Chapter 1, Box 1.2, derives from the principle of identity, since two electrons in one state could not be told apart and so would be one. So electrons crowded together fill their states one to a state, from the lowest up to a top. At the lowest temperature every state below the top is full and every state above it empty: the full states are the *Fermi sea*, and the energy of the top is the *Fermi level* (Chapter 2, Section XII). The more electrons in each unit of volume, the higher the top. In Chapter 6, Box 6.3, I found the Fermi energy of free electrons, the energy at the top measured from the bottom, $E_F = \hbar^2(3\pi^2 n)^{2/3}/(2m_e)$, set by their number n in each unit of volume alone, 7.03 eV for copper. Squeeze the electrons into a smaller room and n rises, so every electron's state is pushed up. The electrons must take states of shorter wave and higher momentum, since confinement costs energy (Volume One, Chapter 7, Section IV). A crowd whose energy rises when it is squeezed pushes back on whatever squeezes it, and that push is a pressure. In Box 13.1 I find its size.

Box 13.1. The pressure of a filled Fermi sea

Premises. (1) N electrons in a volume V, at the lowest temperature, fill every state of motion up to the Fermi energy $E_F = \hbar^2(3\pi^2 n)^{2/3}/(2m_e)$, with $n = N/V$, two electrons to each state of motion, one of each spin (Chapter 6, Boxes 6.2 and 6.3). (2) The number of states up to an energy E grows as $E^{3/2}$ for free particles moving slowly against c (Chapter 6, Section IV, the density of states growing as the square root of the energy), so the average energy of the filled electrons is $(3/5)E_F$ (mathematics). (3) The pressure of a system at the lowest temperature is the fall of its energy for each rise of its volume, $P = -dE/dV$ with N held fixed (standard thermodynamics; Chapter 2, Section XIV). (4) For electrons moving near c, the

energy of a state grows as its momentum times c, and the same filling gives the energy at the top $\hbar c(3\pi^2 n)^{1/3}$ and the average (3/4) of it (standard physics; mathematics).

Steps. By (1) and (2), the total energy is $E = (3/5)N\,E_F$, and E_F goes as $n^{2/3}$, so as $V^{-2/3}$ at fixed N. By (3), $P = -dE/dV = (2/3)E/V = (2/5)nE_F = (3\pi^2)^{2/3}\hbar^2 n^{5/3}/(5m_e)$. By (4), for electrons near c, $E = (3/4)N\hbar c(3\pi^2 n)^{1/3}$, which goes as $V^{-1/3}$, so $P = (1/3)E/V = (3\pi^2)^{1/3}\hbar c n^{4/3}/4$.

Result. A filled Fermi sea presses outward with a pressure that needs no temperature at all, $P = (3\pi^2)^{2/3}\hbar^2 n^{5/3}/(5m)$ for particles of mass m moving slowly against c, and $P = (3\pi^2)^{1/3}\hbar c n^{4/3}/4$ for particles moving near c. The first falls as one over the particles' mass, so in matter of electrons and nuclei it is the electrons, the lightest particles, whose exclusion presses hardest. The second does not depend on the mass, and grows with the squeezing more slowly, as $n^{4/3}$ instead of $n^{5/3}$.

That pressure, which a crowd of fermions exerts because exclusion holds most of them in states above the lowest, is *degeneracy pressure*. In this name the word degenerate means a gas of fermions so crowded that its states are filled from the bottom. A gas of fermions filled from the bottom is the opposite of the classical limit of Chapter 2, Section XII, in which the states are sparsely taken. It is a second use of the word, beside the degeneracy of Volume One, Chapter 7, Section VII, the number of distinct states that share one energy. Degeneracy pressure is the same stiffness that stops a hand on a table, seen in a crowd of free electrons: there it keeps two bodies' atoms apart, and here it keeps a whole star from shrinking. Ralph Fowler saw in 1926 that a white dwarf is held up this way, by its electrons filling their states as fermions, almost as soon as the rule for filling them was found (Fowler, 1926).

So we now know how a crowd of electrons pushes back with no heat in it. Exclusion makes the electrons fill their states from the lowest up, so squeezing them into a smaller room raises every state. The crowd presses

outward with a pressure that would stay at the lowest temperature there is: as $n^{5/3}/m$ for electrons moving slowly, and as $n^{4/3}$, with no mass in it, for electrons moving near c.

III. White Dwarfs

A bag of marbles keeps its size because the marbles touch. A white dwarf has no marbles in it: its atoms are crushed, their electrons torn from their nuclei and shared through the whole star as the free electrons of a metal are shared through the metal (Chapter 6, Section IV). Is the electrons' exclusion enough to hold up a star, and what size does it give one?

Take Sirius B. Its nuclei are mostly carbon and oxygen, which have two nucleons for each electron, so its mean density of 2.77 tonnes in each cubic centimeter gives 8.3×10^{35} electrons in each cubic meter (computed, from the atomic mass unit of Chapter 2, Section X). By Box 13.1 the electrons at the top of that sea have a momentum whose product with c is 0.575 MeV, already more than the electron's rest energy, $m_e c^2 = 0.511$ MeV: they move at a large fraction of the speed of light. At such speeds an electron's whole energy E, its rest energy with its energy of motion, follows from its momentum p by $E^2 = (pc)^2 + (m_e c^2)^2$ (standard physics, the special theory of relativity). So their energy of motion at the top is $(0.575^2 + 0.511^2)^{1/2} - 0.511 = 0.26$ MeV, which as a temperature, the energy divided by the Boltzmann constant, is three billion kelvin (computed). A white dwarf's interior, at some ten million kelvin (standard accounts of white dwarfs), is cold beside that, and its electrons fill their states from the bottom as if at the lowest temperature. Box 13.1 gives their pressure in its two limits, 1.7×10^{22} pascals for slow electrons and 1.9×10^{22} for electrons near c. The electrons at the top of this sea are neither, and the same count of their energy, made with the relation above that holds at every speed, gives about 1.3×10^{22} pascals at the star's mean density, some 10^{17} times the pressure of the air (computed). The nuclei add little. They are fewer, about one for every six electrons in carbon, and at ten million kelvin their heat would

add about a thousandth to the electrons' pressure (computed). And their own exclusion presses far less than the electrons', since by Box 13.1 it falls as one over the mass. So a white dwarf is held up by the degeneracy pressure of its electrons.

The size it settles at is where that pressure balances the star's own gravity, and in Box 13.2 I find the balance in outline. Its first result is strange to anyone who has held a bag of marbles: a heavier white dwarf is smaller. More mass pulls harder, and the electrons can push harder only by being squeezed into a smaller room, so the star shrinks until they do. For electrons moving slowly against c, the radius goes as one over the cube root of the mass. Sirius B, of 1.02 times the Sun's mass, has a radius of about 5,600 kilometers, smaller than the white dwarfs of about 0.6 times the Sun's mass that are most common, which are about the size of the Earth (standard accounts of white dwarfs). And the Sun itself, when it has burned its fuel, will leave a white dwarf (standard accounts of the evolution of stars).

So we now know what holds up a white dwarf. Its electrons, freed from their atoms and crowded far beyond the crowding of a metal, fill their states from the bottom, and their degeneracy pressure, which needs no heat, holds the star against its gravity. The more massive the star, the smaller it settles, and the faster its electrons at the top move.

IV. The Chandrasekhar Mass

Lay one more book on a pile of books, and the pile grows. Lay one more on a sagging shelf, and at some book the shelf gives way all at once. A heavier white dwarf is smaller, so its electrons are squeezed harder and move faster, nearer c. Is there a mass at which the electrons can no longer hold?

There is, and it comes from the change of Box 13.1 between slow electrons and fast ones. For slow electrons the pressure grows as $n^{5/3}$, faster than the squeezing gravity applies, so a star that shrinks a little pushes

back more than it is pressed, and it settles. For electrons near c the pressure grows only as $n^{4/3}$, and gravity's squeeze, as Box 13.2 shows, grows in the same way as the star shrinks. Then shrinking gains the electrons nothing against gravity, and whether the star holds is decided by its mass alone.

Box 13.2. The Chandrasekhar mass in outline

Premises. (1) A white dwarf of mass M and radius R holds $N = M/(\mu_e m_u)$ electrons, with m_u the atomic mass unit and μ_e, read "mu e", the number of nucleons for each electron, 2 for carbon and oxygen; their number in each unit of volume is of order N/R^3 (in outline, numbers of order one dropped). (2) By Box 13.1, the energy of motion of an electron at the top of the sea is of order $\hbar^2 N^{2/3}/(m_e R^2)$ for slow electrons and $\hbar c N^{1/3}/R$ for electrons near c. (3) The star's gravitational energy is of order $-GM^2/R$, with G the constant of gravitation, 6.67430×10^{-11} in the international units (CODATA 2022), so each electron's share is of order $-GM\mu_e m_u/R$ (Newton's law of gravitation; *The Gravitational Passage*, Chapter 16, Section I, recovers it from the field equations). (4) A star settles at the radius of least total energy; if its energy falls without end as R shrinks, no radius holds it (standard physics).

Steps. Slow electrons: by (2) and (3), each electron's energy is of order $\hbar^2 N^{2/3}/(m_e R^2) - GM\mu_e m_u/R$, which has a least value where R is of order $\hbar^2 N^{2/3}/(m_e GM\mu_e m_u)$. With N in proportion to M, R goes as $M^{-1/3}$: a heavier white dwarf is smaller. Fast electrons: each electron's energy is of order $(\hbar c N^{1/3} - GM\mu_e m_u)/R = (\hbar c N^{1/3} - GN(\mu_e m_u)^2)/R$, both parts going as 1/R. If $\hbar c N^{1/3}$ is the larger, the energy is positive and falls as R grows, so the star swells until its electrons slow and it settles as in the slow case. If $GN(\mu_e m_u)^2$ is the larger, the energy is negative and falls without end as R shrinks: by (4), no radius holds the star. The two are equal where $N^{2/3} = \hbar c/(G(\mu_e m_u)^2)$, that is, at the mass $M = (\hbar c/G)^{3/2}/(\mu_e m_u)^2$, in outline. With $\mu_e = 2$, the outline gives 0.47 times the Sun's mass of 1.988×10^{30} kilograms (computed; CODATA 2022 and the solar mass of the Inter-

national Astronomical Union). Solving the structure of the star in full, with its density falling from the center outward, multiplies the outline by 3.10 (Chandrasekhar, 1931; computed from the constant 2.018236 of that solution): 1.46 times the Sun's mass for $\mu_e = 2$.

Result. A star held up by electrons moving near c has a greatest mass, the *Chandrasekhar mass*, about 1.4 times the Sun's mass for matter of two nucleons to each electron: 1.46 for ideal electrons, lowered slightly by small corrections, among them the electric pull between the electrons and the nuclei (Chandrasekhar, 1931; standard accounts of the Chandrasekhar limit). Its size is set by ħ, c, G and the nucleon's mass: in the outline it is $m_{Pl}^3/(\mu_e m_u)^2$, with $m_{Pl} = (\hbar c/G)^{1/2} = 2.18 \times 10^{-8}$ kilograms the *Planck mass*, the mass that ħ, c and G make together; the electron's own mass does not enter.

Subrahmanyan Chandrasekhar found the greatest mass in 1930, on his way by ship from India to England, by adding the speed limit of relativity to Fowler's account, and published it in 1931 (Chandrasekhar, 1931). He received the Nobel Prize in Physics for 1983 (standard accounts of the Chandrasekhar limit). The result says something about every star at once. The mass of a star is a count of nucleons, and the Chandrasekhar mass is about $(m_{Pl}/m_u)^3$ nucleons, 2×10^{57} (computed), against the Sun's 1.2×10^{57} (computed). The natural scale of a star's mass is set by how much weaker gravity is than the other forces, through the Planck mass, and by the nucleon's mass. So every white dwarf lies below the Chandrasekhar mass, as every white dwarf weighed does (standard accounts of white dwarfs). A white dwarf in a close pair of stars can draw matter from its partner up toward that mass. Then it heats in its center until its carbon burns all at once, and the star blows apart in a supernova, an exploding star, of the kind astronomers call Type Ia, whose light shows no hydrogen (standard accounts of the Chandrasekhar limit).

The nucleon's mass is itself set by the strength of color, the charge of the strong force. Color's strength changes with the energy at which it is probed (Chapter 1, Section II): it is weak at the highest energies and grows as the energy falls. Read downward in energy, it reaches a strength of order one at an energy near the proton's mass, and the proton's mass is a fixed multiple of the energy at which it does (The Strengths of the Kinds, Chapter 6, Section II). In that book I start the reading at the reduced Planck mass, the Planck mass divided by $\sqrt{(8\pi)}$, 2.4×10^{18} GeV (computed), where color's measured strength, carried up to that energy by its law of running at the first order of the calculation, its one-loop law, is about 1/50. The rate of that running is set by the number 7, eleven less two-thirds for each of the six kinds of quark, $11 - (2/3) \times 6$ (standard physics, as that book gives it). Run down from the reduced Planck mass, the strength reaches order one after $2\pi \times 50/7 = 44.9$ units of the natural logarithm, a fall of energy by the factor $e^{44.9}$, of the same size as the measured $e^{42.4} = 2.6 \times 10^{18}$ between the reduced Planck mass and the proton's mass (The Strengths of the Kinds, Chapter 6, Box II-1). So the greatest mass a white dwarf can have is tied, through the proton, to the strength of color at the highest energies: the count of about $(m_{Pl}/m_u)^3$ nucleons is the cube of how far the nucleon's mass lies below the Planck mass, and that distance is the one that color's strength fixes.

So we now know that a white dwarf has a greatest mass. As a white dwarf grows heavier it shrinks, its electrons move nearer c, and their pressure grows only as fast as gravity's squeeze. Above about 1.4 times the Sun's mass, the Chandrasekhar mass, set by ħ, c, G and the nucleon's mass, the electrons' exclusion can hold no size against gravity.

V. Electrons Pressed into Protons

In Volume One, Chapter 7, Section X, I fed a banknote into a change machine that pays out only in the note's own currency and only for less, and the note came back unchanged. So a hydrogen atom cannot become a

neutron and a neutrino, because they are heavier than the atom by 0.782 MeV (Volume One, Chapter 7, Box 7.3). Now let the note arrive with a coin taped to it, worth more than the fee. What happens to protons and electrons pressed together so hard that every electron arrives carrying energy?

In a squeezed sea of electrons, the electrons at the top carry the Fermi energy, and nothing can take it from them, since every state below theirs is full. The change $p + e^- \rightarrow n + \nu_e$, electron capture (Chapter 12, Section XIV), is closed for an electron at rest by 0.782 MeV. For an electron that brings 0.782 MeV of energy of motion with it, it opens. Counted with the electron's rest energy of 0.511 MeV, that is a whole energy of 1.293 MeV for the electron, the neutron's excess over the proton, since 0.782 MeV and 0.511 MeV together make 1.293 MeV. For a sea of electrons among free protons, the electrons at the top reach that whole energy when there are 7.4×10^{36} electrons in each cubic meter, by Box 13.1 with the relation of energy to momentum of Section III, a density of about 1.2×10^7 grams in each cubic centimeter of hydrogen (computed). For protons bound in heavier nuclei the capture costs more, since it must also pay for the change of binding, and it opens at higher densities. Exclusion supplies the energy that hydrogen lacks: the electrons are pressed into the protons, and the protons become neutrons.

Once made, the neutrons last. A free neutron decays in about fifteen minutes into a proton, an electron and an antineutrino, setting free 0.782 MeV (Volume One, Chapter 3, Section IV). In the squeezed matter the electron that decay would make must take an empty state, and every electron state up to the Fermi energy is full. Once the Fermi energy is larger than all that the decay could give its electron, there is no empty state for the electron to take, and the decay cannot happen. So the neutrons last, held by exclusion, as neutrons inside nuclei last for a reason of their own, the cost of the new proton (Volume One, Chapter 5, Section V).

The matter settles where turning a neutron into a proton and an electron gains nothing, and turning a proton and an electron into a neutron gains nothing either. Each kind of particle has its chemical potential, the energy that adding one more particle of that kind brings to the system when its entropy, the logarithm of the number of its microstates, and its volume are held fixed (Chapter 2, Sections III and XI). The settled matter has the neutron's chemical potential equal to the proton's and the electron's together, with as many electrons as protons, since the matter carries no net charge. For free particles at the density of a nucleus that balance leaves about one proton for every two hundred neutrons (computed, from the Fermi seas of the three kinds). The force between nucleons, which in nuclei favors equal numbers of protons and neutrons by the asymmetry term of Volume One, Chapter 4, Section VII, raises the share of protons above that. So matter pressed hard enough becomes mostly neutrons, with a few protons and as many electrons among them.

Matter is pressed hard enough to become mostly neutrons at the center of a massive star, at the end of the star's life. In Volume One, Chapter 6, Section IV, I found that a star of many times the Sun's mass burns its fuels up to iron, which can burn no further. I found too that the iron core, with nothing to hold it up, collapses in less than a second into a neutron star or a black hole as the star explodes. The iron core is held up by its electrons, as a white dwarf is. When its mass grows past what they can hold, the core falls in, and as it falls its electrons are pressed into its protons, which takes away the very electrons whose pressure held it, and the collapse runs on until the matter is mostly neutrons.

So we now know how electrons are pressed into protons. In matter squeezed far enough, the electrons at the top of their sea carry more than the 0.782 MeV that keeps hydrogen from becoming a neutron, so they are captured by the protons, which become neutrons. The neutrons then last, because their decay would need an empty electron state and there is none below the Fermi energy. And matter so pressed settles as mostly neutrons.

VI. What the Force Between Nucleons Adds

In Volume One, Chapter 4, Section V, I wrapped two magnets each in a woolen sock: they pull together from across the table, but the socks stop them short, and they rest at the separation where pull and stop balance. Nucleons in a nucleus rest the same way, at a fixed density. A neutron star presses its neutrons together harder than a nucleus does. What holds it up?

Two things hold it up, one of them exclusion, the rule that holds up a white dwarf. Neutrons are fermions, of spin one half, so they too fill their states from the lowest up and press outward by Box 13.1. At the density of a nucleus, about 0.16 nucleons in each cubic femtometer (Volume One, Chapter 4, Section VI), neutrons alone would fill their states up to a Fermi energy of 58 MeV. Their degeneracy pressure would be about 6×10^{32} pascals (computed, Box 13.1 with the neutron's mass). The neutron is 1839 times heavier than the electron, so at the same density its exclusion presses 1839 times less hard. But a neutron star is a hundred million times denser than a white dwarf, and the pressure grows as the density to the power 5/3.

The second thing that holds a neutron star up is the force between nucleons. In a nucleus that force sets the density. It pulls nucleons together from about the pion's reach, 1.41 fm, and pushes them apart when they are pressed closer than about half a femtometer, the repulsive core (Volume One, Chapter 4, Sections IV and V). The two balance at the density each nucleus has, since each nucleon holds only its neighbors (Volume One, Chapter 4, Section VI). At that density the force between nucleons adds no pressure of its own in a nucleus, which is why a nucleus keeps its size. A neutron star's center is pressed past it. There the neutrons, 1.84 femtometers apart at a nucleus's density (computed), are pushed closer, toward the repulsive core, and the core's push adds to the neutrons' exclusion. And matter of neutrons alone is less bound than a nucleus with

equal numbers of protons and neutrons, by the asymmetry term of Volume One, Chapter 4, Section VII, the cost of so many neutrons with so few protons. That cost for each neutron grows as the neutrons are squeezed closer (standard nuclear physics), and an energy that grows with squeezing pushes outward (Box 13.1, premise 3), so the cost of so many neutrons adds a further pressure. So the matter of a neutron star is far stiffer than neutrons' exclusion alone would make it.

The heaviest neutron stars weighed show how stiff. A *pulsar* is a spinning neutron star whose beams of radio waves sweep past the Earth at each turn, and in the In Use section I follow pulsars further. The pulsar PSR J0740+6620, its name the letters for a pulsar followed by its place in the sky, circles with a white dwarf. Light, and radio waves with it, is delayed in passing a mass: *The Gravitational Passage*, Chapter 16, Section III, names "the Shapiro time delay" among the well-known features of the field of gravitation outside a mass. So the pulsar has been weighed by the delay its radio pulses suffer in passing its partner's pull, which gives the partner's mass and, with the orbit, the pulsar's own: 2.08 ± 0.07 times the Sun's mass (Fonseca et al., 2021), far above the Chandrasekhar mass. Its radius, measured from the X-rays of hot spots on its surface, is 13.7 kilometers, with an uncertainty of 2.6 kilometers above and 1.5 below (Miller et al., 2021). Its mean density is then about 3.8×10^{17} kilograms in each cubic meter, about 1.4 times the density of a nucleus (computed): a teaspoon of it would weigh about two billion tonnes. And it is compact in a second sense. *The Gravitational Passage*, Chapter 16, Section III, gives the radius of the horizon of a mass M, the bound from inside which nothing, not even light, can leave: the *Schwarzschild radius*, $r_s = 2G_N M/c^2$, with G_N the constant of gravitation, the G of Box 13.2. For 2.08 times the Sun's mass it is 6.1 kilometers (computed), so this neutron star's radius is only about 2.2 times the radius its horizon would have if its mass were packed within it. The two neutron stars that merged in the event GW170817 had

masses between 1.17 and 1.60 times the Sun's (LIGO Scientific Collaboration and Virgo Collaboration, Abbott et al., 2017), and most neutron stars weighed lie near 1.4 (standard accounts of neutron stars).

A neutron star is built in layers. In its outer layers, where the pressure is lower, nuclei survive, rich in neutrons, in a crystal among the electrons, a crust. Deeper, neutrons drip out of the nuclei, as they do past the neutron drip line of Volume One, Chapter 5, Section IX. Deeper still the nuclei dissolve into a fluid of neutrons with a few protons and electrons (standard accounts of neutron stars). The nucleus, which hid inside its atom in Chapter 12, is here the matter of the whole star. It holds about 10^{57} nucleons at about a nucleus's density, held together by gravity, with too few protons for the electric push that splits the heaviest ordinary nuclei (Volume One, Chapter 5, Section XI).

So we now know what holds up a neutron star. Its neutrons' exclusion presses outward as the electrons' does in a white dwarf, and where the star presses its neutrons closer than in a nucleus, the force between nucleons adds the push of its repulsive core and the cost of so many neutrons. The matter is stiff enough to hold more than twice the Sun's mass within a radius only about twice its horizon's.

VII. Where Pressure Ends

The ladder of this book has been a ladder of things that hold: quarks held into nucleons, nucleons into nuclei, nuclei and electrons into atoms, atoms into molecules and crystals, and now, under the weight of a star, electrons and then neutrons holding by their exclusion. What becomes of a star whose matter is more than its pressure holds?

Exclusion and the force between nucleons hold up every white dwarf and every neutron star: the white dwarfs below the Chandrasekhar mass, and the neutron stars, the heaviest weighed being PSR J0740+6620, of 2.08

times the Sun's mass. A body pressed beyond what its matter's pressure holds belongs to the account of gravitation, and *The Gravitational Passage* gives that account in three statements.

The first says where such bodies go. Of all the matter that can ever reach an observer, it states: "Stars form, burn out and leave remnants; remnants accrete and merge; bound structures end in black holes" (*The Gravitational Passage*, Chapter 18, Section III). The remnants are the white dwarfs and neutron stars of this chapter, and to accrete is to draw in matter from round about, as the white dwarf of Section IV draws matter from its partner. A *black hole* is a body whose gravity lets nothing out, not even light (Volume One, Chapter 6, Section IV).

The second says how large a black hole is. In *The Gravitational Passage* I place its horizon, the bound from inside which nothing can leave, at the Schwarzschild radius $r_s = 2G_N M/c^2$ for a body of mass M (Chapter 16, Section III). For a mass like the Sun's that is about three kilometers (computed), and in Section VI I found that the heaviest neutron star weighed is only about 2.2 times larger than its own horizon would be.

The third says what becomes of what falls in. "Inside the horizon of a non-rotating hole, the radial direction is the direction of time. The singularity is therefore a moment, not a place at the center: the future end of every path inside the horizon" (*The Gravitational Passage*, Chapter 18, Section I). So inside the horizon the way inward is the way forward in time, and no path can turn back out, as no one can turn back to yesterday. The end of every such path is a moment, a limit that the path approaches and does not reach, and for a black hole of one solar mass it comes "at most about fifteen microseconds after the crossing" (same section). What lies inside the horizon belongs to *The Gravitational Passage*, where I trace it in its Chapters 18 and 19.

So we now know what becomes of a star whose matter is more than its pressure holds. Its matter ends in a black hole, a body whose gravity lets nothing out from inside its horizon at $r_s = 2G_N M/c^2$. Every path that crosses that horizon comes, in a short time, to its end at a moment, as *The Gravitational Passage* states.

In Use

In 1967 Jocelyn Bell, a student at Cambridge, found in the record of a new radio telescope a source that pulsed every 1.34 seconds, as steadily as a clock. With Antony Hewish and their colleagues she reported it in 1968 (Hewish et al., 1968; standard accounts of pulsars). Thomas Gold argued the same year that such a source is a spinning neutron star. Its magnetic field sends out beams of radio waves from its magnetic poles, and as the star turns the beams sweep past the Earth like the beam of a lighthouse (standard accounts of pulsars). A neutron star can spin so fast because it is so small. The core of a star that collapses keeps its angular momentum, the quantity kept because the laws are the same in every direction (Volume One, Chapter 7, Section VI). As its radius falls from the thousands of kilometers of a white dwarf (Section III) to some thirteen, about the radius measured for PSR J0740+6620 (Section VI), it spins up as a skater spins faster on drawing in her arms. The pulsar at the heart of the Crab Nebula, the remnant of a supernova seen in the year 1054, turns once every 33 milliseconds, and the fastest pulsar known turns 716 times a second (standard accounts of pulsars).

Pulsars are clocks. The fastest, the millisecond pulsars, turn so steadily that their pulses can be timed against the atomic clocks of Chapter 12, Section XV, as clocks of comparable steadiness (standard accounts of pulsars). Russell Hulse and Joseph Taylor found in 1974 a pulsar circling another neutron star every 7.75 hours (Hulse and Taylor, 1975). Timing its pulses over the years showed the orbit shrinking exactly as the Einstein equations of gravitation (Chapter 11, Section XI) require of two stars that

lose energy to gravitational waves (Volume One, Chapter 6, Section VI). Gravitational waves are ripples in the shape of space and time, and they carry energy away. Hulse and Taylor received the Nobel Prize in Physics for 1993 (standard accounts of pulsars). And timing many pulsars together turns the galaxy into a detector. The North American Nanohertz Observatory for Gravitational Waves (NANOGrav), timing 67 pulsars for 15 years, found the pattern of correlations that a background of gravitational waves passing through the galaxy makes in the pulses' arrival times (NANOGrav Collaboration, Agazie et al., 2023).

Two neutron stars circling each other lose energy to gravitational waves until they spiral together and merge. On 17 August 2017 the two detectors of the Laser Interferometer Gravitational-Wave Observatory (LIGO) and the Virgo detector caught the gravitational waves of such a merger, GW170817 (LIGO Scientific Collaboration and Virgo Collaboration, Abbott et al., 2017). The two stars had about 2.74 times the Sun's mass together and lay some 40 megaparsecs away (LIGO Scientific Collaboration and Virgo Collaboration, Abbott et al., 2017). A megaparsec is about 3.26 million light years, a light year being the distance light travels in a year, about 9.46×10^{15} meters (computed). A burst of gamma rays arrived from the same place about 1.74 seconds after the waves (LIGO Scientific Collaboration, Virgo Collaboration, Fermi GBM and INTEGRAL, Abbott et al., 2017). So the waves and the light came from one event, a merger of neutron stars, and after traveling for some 130 million years the waves and the light arrived together. Gravitational waves travel at the speed of light, to within a few parts in 10^{15} (*The Gravitational Passage*, Chapter 16, Section V). In Volume One, Chapter 6, Section VI, I found what the merger made. Neutron-rich matter thrown out of the merging stars built heavy nuclei in about a second by the rapid capture of neutrons. Its glow, a kilonova, faded and reddened as freshly made nuclei were expected to make it, and strontium was identified in its light. So mergers of neutron stars are one place where the heaviest elements are made, and the gold of a ring may well have been made in one. The matter

of this chapter, pressed until its protons had taken in its electrons and become neutrons, is thrown back out and becomes, within about a second, the heavy nuclei of the elements of Volume One.

Summary

A white dwarf and a neutron star are held up by exclusion. Electrons crowded together fill their states from the lowest up, so squeezing them raises every state. The crowd presses outward with a degeneracy pressure that needs no heat: as $n^{5/3}/m$ for particles moving slowly, so that the lightest, the electrons, press hardest, and as $n^{4/3}$ for particles near c (Box 13.1). A white dwarf, the cooling remnant of a star of about the Sun's mass, with Sirius B's mass of 1.02 times the Sun's in a radius of about 5,600 kilometers, is held up by its electrons' degeneracy pressure, and a heavier white dwarf is smaller. In the heaviest, the electrons move near c and their pressure grows only as fast as gravity's squeeze, so above the Chandrasekhar mass, about 1.4 times the Sun's, made of ħ, c, G and the nucleon's mass, no size holds (Box 13.2).

Pressed further, the electrons at the top of their sea carry more than the 0.782 MeV that keeps hydrogen from becoming a neutron, and they are pressed into the protons, which become neutrons. The neutrons last, since their decay would need an empty electron state and none is left below the Fermi energy, and matter so pressed settles as mostly neutrons. A neutron star is matter at about a nucleus's density, held up by its neutrons' exclusion and, where it is pressed closer than a nucleus, by the push of the force between nucleons. The heaviest weighed, 2.08 times the Sun's mass, lies within about 2.2 times the radius of its horizon. Beyond what its matter's pressure holds, a body belongs to the account of gravitation, and *The Gravitational Passage* states that bound structures end in black holes. Spinning neutron stars are pulsars, clocks that rival atomic clocks and that have shown gravitational waves at work. Merging neutron stars send out gravitational waves and make the heaviest elements.

The chapter's one rule is the first rule of the kinds, exclusion, carried from the atom to the star. The same rule that gives atoms their shells and stops a hand pressed on a table gives white dwarfs their size and their greatest mass, with gravity in place of the push of a hand. The degeneracy pressure and the Chandrasekhar mass follow from exclusion with ħ, c, G and the particles' masses. The force between nucleons makes matter denser than a nucleus stiffer, through its repulsive core and the cost of so many neutrons. How much stiffer is read from the stars themselves, as are the masses and radii of particular stars.

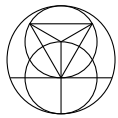
The ladder has now been climbed from the proton to the neutron star, and every rung, held by what the one below leaves over, has been found to be shaped by the two rules of the kinds, exclusion and the counting of angular momentum in steps of ħ. Looking back over the ladder, what do the wholes make?

✶

KEY CONCEPTS

- **White dwarf.** The cooling remnant of a star that has burned its fuel, about as massive as the Sun and about as large as the Earth, held up by its electrons' degeneracy pressure.
- **Degeneracy pressure.** The pressure a crowd of fermions exerts because exclusion holds most of them in states above the lowest; it needs no heat, and goes as $n^{5/3}/m$ for particles moving slowly and as $n^{4/3}$ for particles near c (Box 13.1).
- **Chandrasekhar mass.** The greatest mass that electrons' degeneracy pressure can hold up, about 1.4 times the Sun's mass for matter of two nucleons to each electron, set by ħ, c, G and the nucleon's mass (Box 13.2).
- **Planck mass.** $(\hbar c/G)^{1/2}$, 2.18×10^{-8} kilograms, the mass that ħ, c and the constant of gravitation make together.

- **Electrons pressed into protons.** In matter squeezed far enough, the electrons at the top of their sea carry more than 0.782 MeV, so electron capture turns protons into neutrons, and exclusion keeps the neutrons from decaying.
- **Neutron star.** Matter at about the density of a nucleus, mostly neutrons, held up by their exclusion and by the push of the force between nucleons where they are pressed closer than in a nucleus.
- **Schwarzschild radius.** The radius of the horizon of a mass M, the bound from inside which nothing can leave, $r_s = 2G_N M/c^2$ (*The Gravitational Passage*, Chapter 16, Section III).
- **Pulsar.** A spinning neutron star whose beams of radio waves sweep past the Earth at each turn, timed as a clock.



Chapter 14

What the Wholes Make

CHAPTER OVERVIEW

This chapter gathers what both volumes found, so that the whole ladder, from the proton to the solid and the star, can be seen at once. Volume One followed the wholes one at a time, quarks into nucleons, nucleons into nuclei, nuclei and electrons into atoms, atoms into molecules, each held by what the level below leaves over and far more weakly than the one below. This volume followed very many wholes together, and each chapter's question and arrival is restated here, rung by rung. On the rung of gatherings no further remainder of a force appears. The gatherings are held by the bonds of Volume One and by the feeble pulls between molecules, and what is new is the number of wholes. With number comes the counting of ways that decides which arrangement the wholes take at each temperature, and the orders that belong to the whole gathering: a repeat, a held direction and a shared phase. The two rules of the kinds, exclusion and the units of angular momentum, work on every rung. Exclusion fills states from the bottom, makes bonds pairs, makes metals and insulators and holds up stars, while even wholes and photons gather into one state. And angular momentum comes in whole units of ħ for a path and in halves for spin one half, from the shells of atoms to the flux through a superconducting ring. Each energy of the ladder, set against the temperature as an energy, kT, decides what heat does to it, and so which machines work at room temperature and which must be cooled (Box 14.1, Table 14.1). Structure fixes the whole numbers that matter keeps, measured

> values fix which case each substance is, and history fixes how much of each element there is and which allowed state a piece of matter keeps when it has not reached its balance. With *The Coming of the Kinds*, the two volumes make one account of the kinds and of what they make.

I. Looking Back over the Ladder

Hold a telephone in your hand. Its screen is glass, a solid whose molecules are caught in the disordered arrangement of a liquid, with a coating that conducts and yet lets light through. Behind the glass, a chip of silicon holds billions of switches, each a junction of silicon with a few atoms of phosphorus or boron set into it on purpose. A battery drives a current by letting lithium give up its outer electron. Small magnets hold their direction in its speaker, a camera turns light into current, and its clock is kept true by atomic clocks in orbit. Each of these parts is a gathering of wholes, and every chapter of the two volumes is at work somewhere in it.

Chapter 13 ended with the ladder climbed from the proton to the neutron star, and with a question: looking back over the ladder, what do the wholes make? In this chapter I answer it for both volumes together, as in Volume One, Chapter 12, I answered for the wholes alone. The answer comes in six parts. The first of the six parts is the ladder rung by rung, with each chapter's question and arrival, first for the wholes of Volume One (Section II) and then for the gatherings of this volume (Section III). Each finding there is stated as its chapter found it, and the reasoning for it is in the chapter named. The other five parts are what is new when the wholes are many (Section IV), the two rules of the kinds on every rung (Section V), the energies of the rungs and what they make possible (Section VI), where structure ends and history begins (Section VII), and what these two volumes and *The Coming of the Kinds* say together about the kinds and what they make (Section VIII).

II. The Wholes, One at a Time

Volume One followed the wholes one at a time, from the bottom of the ladder up. Its Chapter 1 asked what was there when the first atoms had formed, and what the kinds can make. It found that the universe, at about 370,000 years, held nuclei of hydrogen and helium-4 with traces of deuterium, helium-3 and lithium-7, an electron for each proton, the light set free and a sea of neutrinos (*The Coming of the Kinds*, Chapters 12 and 13). It found the kinds of particle a closed list with measured masses, of which ordinary matter uses the few that last. A particle lasts when it is the lightest thing that carries its counts, the electric charge, baryon number and lepton number that every change at the temperatures of the present universe keeps. A carrier of mass m reaches about $\hbar/(mc)$, so that electromagnetism reaches without bound and the weak force about 2.5×10^{-18} m, while the color field is confined. And two rules shape every whole: exclusion, and angular momentum in whole units of $\hbar$ and in halves (this volume, Chapter 1, restates them in Boxes 1.1 to 1.3).

Volume One, Chapter 2, asked what a proton is made of, and why a quark is never found alone. It found that every whole of quarks carries no color, so that counting color gives the meson, a quark with an antiquark, and the baryon, three quarks one of each color, as the wholes of fewest parts. The proton is two up quarks and a down, and the neutron two downs and an up. The color field between quarks pulled apart gathers into a tube whose energy grows until it breaks into a new quark and antiquark, so no quark is found alone. And about 99 percent of the proton's mass is the energy of its binding. Chapter 3 asked why the neutron is heavier, and why that decides which atoms can exist. It found the neutron heavier by 1.293 MeV, a balance of the down quark's extra mass against the proton's extra electric energy. The free neutron decays, with a mean life of 878.3 ± 0.4 seconds, about fourteen and a half minutes (the Particle

Data Group's average), while the proton, the lightest baryon, lasts. And the excess lies above the electron's mass, so hydrogen lasts, and below the binding of nuclei, so neutrons can last inside them.

Chapter 4 asked what holds protons together against their push. It found that to the strong force the proton and the neutron are one nucleon. The force between nucleons is the colorless leftover of the color field, carried by mesons and reaching about 1.41 fm. Each nucleon holds only its neighbors, so every nucleus has one density. The binding peaks at about 8.8 MeV for each nucleon near iron and nickel, so fusion of light nuclei and fission of heavy ones both set energy free. The deuteron is the only bound pair of nucleons, and nucleons fill shells that close at 2, 8, 20, 28, 50, 82 and 126. Chapter 5 asked why there are about 250 stable nuclei, and how the others change. It found that a nucleus lasts when no products with the same counts, the counts that every change at the temperatures of the present universe keeps, have less mass, and that 251 nuclei do. Beta decay rolls nuclei down a bowl of mass at each mass number to the valley of stability, the line of the lightest nucleus of each mass number, and neutrons last inside nuclei on the valley floor. No nucleus of mass 5 or 8 lasts. And alpha decay goes through the electric barrier by *tunneling*, a particle's crossing of a barrier with less energy than the barrier, because its wave extends past the region in which it is confined. Chapter 6 asked how carbon, oxygen, iron and uranium were made. It found that the building of nuclei in the first minutes stopped at the gaps at masses 5 and 8. Stars burn hydrogen, then helium by way of an excited state of carbon-12, then heavier fuels up to iron, crossing their electric barriers by tunneling. And the nuclei beyond iron are built by taking in neutrons, slowly in red giants, stars swollen late in their lives, and rapidly where neutron stars merge.

Chapter 7 asked why an atom has the size it has, and why the electron does not fall in. It found that the ground state, the atom's state of least energy, sends nothing out. Hydrogen's size is where the cost of confinement, $\hbar^2/(2mr^2)$ for a particle of mass m held within a distance r, balances the electric pull, at the Bohr radius, 0.529×10^{-10} m. That cost comes from the

uncertainty principle, an instance of the Incommensuration Theorem, and the balance binds hydrogen's electron by 13.6 eV. Orbital angular momentum comes in whole units of ħ, zero included, because the angle about the proton closes after one turn, while spin comes in halves. The levels are separate, at the Rydberg energy, 13.6 eV, divided by n^2 below the top, and the light comes in sharp lines. And hydrogen lasts because a neutron with a neutrino is heavier than a hydrogen atom by 0.782 MeV. Chapter 8 asked what splits hydrogen's levels, and what the splittings measure. It found four splittings of decreasing size, each measuring something. They are the electron's magnet meeting its orbit, which measures α; the electron's own field acting back on it, which lifts some levels slightly, the Lamb shift; the proton's magnet, the 21 cm line; and the proton's size.

Chapter 9 asked why the periodic table has the shape it has. It found that the inverse-square pull gives shells of 2, 8, 18 and 32 states, and that exclusion fills them from the bottom. Screening lifts the subshells of larger orbital angular momentum, so that they fill in order of n + l, the shell's number added to the orbital angular momentum, the lower sum first, and the periods hold 2, 8, 8, 18, 18, 32 and 32 elements. Closed subshells make the noble gases, loose outer electrons the alkali metals, and aligned spins the magnetic atoms. Chapter 10 asked why gold is yellow and mercury liquid, and where the periodic table ends. It found that the innermost electron moves at about Zα times the speed of light, so that in the heaviest atoms the s states draw in and the d and f states swell, narrowing gold's gap to about 2.4 eV and drawing mercury's outer pair out of its bonds. Atoms would end near Z = 137 for a point nucleus and near 170 to 173 for a nucleus of its true size, but nuclei end first, the heaviest made being oganesson, Z = 118. Chapter 11 asked what a chemical bond is. It found that an electron held by two nuclei has a lower state in which its two parts add between the nuclei, which holds them at the bond length, and that each bond is completed by a pair of electrons of opposite spin in it. Closed shells push apart. Each atom forms as many bonds of an electron pair as the smaller of two numbers, its outer electrons and the electrons it lacks to complete its subshell, pointing as the directions of space allow. Unequal

sharing becomes at the extreme the electron passed over, as in salt, and sharing among many the metallic bond. Every two atoms attract by the feeble dispersion force, and a hydrogen left nearly bare draws a lone pair by the hydrogen bond. And every bond's energy is a fraction of the Rydberg energy, $\alpha^2 m_e c^2/2$, about 13.6 eV: 1 to 10 eV.

Volume One, Chapter 12, set those rungs side by side and found three things that hold on every one. The first of the three things that hold on every rung is that each level is held by what the level below leaves over. Between nucleons, between atoms and between molecules that is a remainder of the force that made the level below, acting only between wholes that nearly touch, and from the nucleus to its electrons it is the whole charge of the nucleus's protons, whose pull reaches without bound. The second thing that holds on every rung is that each level is held far more weakly than the level below. Nuclear energies are about a million times chemical ones, to within a factor of a few, because the cost of confinement, $\hbar^2/(2mr^2)$, grows as one over the square of the region and only as one over the mass. A nucleon is confined to a region some thirty thousand times narrower than an electron in an atom, which enters squared and outweighs its 1836 times greater mass: about 6.1 MeV for a nucleon against 13.6 eV for an electron (Volume One, Chapter 12, Box 12.1). The third thing that holds on every rung is that which wholes exist is structure, which wholes last is structure and measured values, and how many wholes there are is history. Its last question was the question of this volume: what do very many wholes do together?

III. The Gatherings, Very Many at Once

This volume took up that question. Its Chapter 1 asked what Volume One found, and what is needed from it here, and restated it: the kinds and their reach, the ladder, exclusion and the whole and half units of angular momentum in their boxes, the atom's size and levels, the periodic table's

families, the four kinds of bond, and the nucleus with its spin. Its last line was a glass of water that holds about 10^{25} molecules, and the question how anything can be said about so many.

Chapter 2 asked what temperature and entropy are, and why heat flows only one way. It found that every microstate of a system, every complete arrangement of its particles, that has the system's totals counts alike, which follows from the weight its motion keeps and the principle of identity. *Entropy* is the logarithm of the number of a system's microstates with its totals. Almost all of those microstates lie near the arrangement of greatest entropy, and the second law, that the entropy of an isolated system does not decrease, is the one direction of time seen as a count. *Temperature* is the energy it takes to raise a system's entropy by one unit, so heat flows from hotter to colder and no engine turns all its heat into work. The Boltzmann constant, which turns a temperature into an energy, kT, is a unit. A small part of a large system takes each state with the weight $e^{-E/kT}$, the *Boltzmann factor*. With exclusion that weight gives the two kinds of filling, fermions one to a state up to a top and bosons gathering in the lowest state, and light in a box gives Planck's spectrum. A system held at a fixed temperature settles where its energy less its temperature times its entropy, its free energy, is least. So order usually wins when cold and disorder when warm, sharply at a point only where a symmetry or a jump separates the two.

Chapter 3 asked why some reactions go at once and others not at all. It found two routes past a barrier: over the top, at a rate that falls as $e^{-E_a/kT}$ with the barrier E_a and so rises steeply with temperature, the route of most chemistry; and through it, by tunneling, for light movers and in the cold. Where a reaction settles is a separate matter, the law of mass action set by the reaction's free energy. A catalyst lowers the barrier both ways and leaves where it settles unchanged. And the passing of electrons between atoms, set apart in a cell, drives a current at a voltage set by that same free energy. Chapter 4 asked what the phases of matter are, and what lies between solid and liquid. It found that a substance takes the

phase of least free energy for each molecule at its temperature and pressure: a gas whose pressure is the number of molecules in each unit of volume times kT, a liquid whose molecules touch, and the lines, triple point and critical point of the map of the phases. Water's hydrogen bonds hold ice open, so ice floats, and a glass is a liquid cooled too fast to find its rows. Between solid and liquid lie polymers, liquid crystals, colloids and gels, with plasma beyond the gas.

Chapter 5 asked why cool atoms arrange themselves in repeating patterns, and why some solids bend while others break. It found that atoms of one kind differ only by where they are, by the principle of identity, and the laws are the same at every place. So the arrangement of least energy is one arrangement repeated, a *crystal*, a solid whose atoms stand in one arrangement repeated through space. A repeat can be turned onto itself only by a half, a third, a quarter or a sixth of a turn, so there are 14 kinds of lattice and 230 space groups. The atoms vibrate in quanta, phonons, each a quantum of vibration of the crystal's lattice, which are not excluded. And metals bend because their bond has no direction and a crystal slips a row at a time, while covalent solids break and ionic ones split cleanly. Chapter 6 asked why metals conduct, insulators not, and semiconductors a little. It found that the states of an electron in a repeating crystal can be chosen to be the same in every cell up to a phase that moves on by the same amount from cell to cell, Bloch's theorem. Each state of the single atom becomes a *band*, the set of electron states in a crystal that grow from one state of the single atom, which takes two electrons for each cell of the repeat. A solid whose filling stops inside a band is a metal, and one whose filling stops at a full band with a gap above is an insulator. An odd count of electrons for each cell always leaves a band partly filled unless the electrons' push holds each at its atom. A small gap makes a semiconductor, whose carriers heat lifts across in numbers set by the Boltzmann factor, and a perfect, motionless crystal offers no resistance. Chapter 7 asked how a diode passes current one way, and how a transistor switches. It found that an added atom of phosphorus holds its extra electron as a hydrogen atom lessened by the crystal, bound by a few hundredths of an electron

volt, so heat frees it. Where p-type silicon meets n-type a barrier forms, which a forward voltage lowers so that the current grows by the Boltzmann factor. A voltage on a gate draws a channel that switches a transistor, and a junction gives out light at the color of its gap and turns light into current.

Chapter 8 asked why iron is a magnet and copper not, and why heat destroys a magnet. It found that every electron is a magnet of one Bohr magneton and an atom carries a net moment only with a partly filled subshell. Between neighbors the electric push, sorted by the spins through exclusion, lines the moments up in iron and alternates them in other crystals. The laws treat every direction alike, and the aligned crystal picks one easy direction and holds it, the pick being held by the whole crystal: *spontaneous symmetry breaking*, a symmetry of the laws that the state of least energy does not share. Heat raises the entropy of unaligned arrangements, so the alignment is lost at the Curie point, 1043 kelvin for iron, and large magnets divide into domains. The Higgs field shares the magnet's structure, but no measurement can tell one of its picks from another, and its mass lies far above the one below which its settling would jump, and so it settled in a crossover, a smooth change with no jump. Chapter 9 asked how a liquid can flow without friction and a metal carry current without loss. It found that wholes of an even number of particles of spin one half, not excluded, gather when cold and crowded into one state, a *condensate*, a gathering of many wholes into one state with one amplitude and one phase. Such a gathering, when its wholes push one another, flows without loss at any speed below the least ratio of energy to momentum among the motions that could slow it. Helium-4, six particles of spin one half, gathers at 2.17 kelvin, while helium-3, five, waits until its atoms pair. Electrons in a metal pair through the lattice under any pull because the states below them are taken, and the pairs share one phase, so a current, a twist of that phase, meets no resistance. And the shared state of charged pairs gives the photon a mass inside the metal and keeps out a magnetic field, the Higgs field's way of giving a carrier its mass, seen again in a metal. Chapter 10 asked how a material can measure a constant of nature to ten decimal

places. It found that the shared phase of a superconductor's pairs, each of charge 2e, must come back to itself round a ring, so the ring traps magnetic flux only in whole units of h/2e. Across a junction of two superconductors a voltage makes the current swing at 2eV/h in every material. A sheet of electrons in a strong field holds its Hall resistance at $h/(\nu e^2)$ with ν a whole number, because the conductance is a winding that no smooth change alters. And the Planck constant and the electron's charge are values while the factors by which they enter are fixed by structure, which is why the volt and the ohm are the same in every laboratory.

Chapter 11 asked why light is slower in glass, when its speed never changes. It found that a passing wave sets every bound electron swinging, and that each electron's wave is a quarter cycle behind the wave that drives it. The sum of the waves, every wave in it traveling at c, has its crests delayed, so its phase advances at c/n, n being the *refractive index*. From that sum came refraction, reflection, colors parting, the blue of the sky, the two polarizations, the shine of metals, light passing through light, and the laser, which multiplies light because photons are not excluded. Chapter 12 asked how a hospital scanner sees the nucleus that chemistry ignores. It found that the nucleus hides because it is heavy and small, and shows through in five places. The first of the five places is isotopes, whose light is shifted and whose heavier forms react more slowly, by the lower zero-point energy of the heavier forms. The second place is the nucleus's spin, which makes the nucleus a magnet whose orientations in a field differ by an energy in proportion to the field: nuclear magnetic resonance. The third place is gamma rays given off without recoil by a crystal, and the fourth place is the few decays that depend on the electrons. The fifth is clocks: atoms of one kind cannot be told apart, so the frequency of any of their transitions is a standard of time. Chapter 13 asked what holds up a white dwarf and a neutron star. It found that exclusion fills a crowd of fermions from the bottom, so squeezing raises every state and the crowd presses outward with a pressure that needs no heat. A white dwarf is held up by its electrons, and above the Chandrasekhar mass, about 1.4 times the Sun's, made of $\hbar$, c, the constant of gravitation and the nucleon's mass,

no size holds. Pressed further, the electrons bring the 0.782 MeV that hydrogen lacks and become neutrons with the protons. And a neutron star is held up by its neutrons' exclusion and the push of the force between nucleons, and beyond what they hold, a star's matter ends in a black hole, as *The Gravitational Passage* states.

Read together, the two volumes climb one ladder: quarks into nucleons, nucleons into nuclei, nuclei and electrons into atoms, atoms into molecules, and molecules and atoms into gases, liquids, crystals, metals, semiconductors, magnets, condensates and stars.

IV. What Is New When the Wholes Are Many

One coin poured from a cup shows heads or tails. A hundred coins poured together show roughly half heads (Chapter 2, Section I). "Roughly half" is a fact about the hundred that no single coin has, and it comes from counting the ways the hundred can fall.

Up the ladder of Volume One, each rung was held by what the rung below left over: the colorless leftover of the color field, the whole charge of the nucleus, the atom's outer electrons and its passing separations of charge (Volume One, Chapter 12, Section III). Past the molecule, no further remainder appears. The gatherings of this volume are held by the bonds and the feeble pulls between molecules that Volume One already found: a covalent crystal by its shared pairs, a salt by the electric pull between its ions, a metal by its shared outer electrons, and a liquid or a molecular solid by the dispersion force and the hydrogen bond (Chapter 1, Section VIII; Chapter 5, Section VI). Even the orders among many come from the same electric pull and push: the alignment of a magnet from the push between electrons, sorted by their spins through exclusion (Chapter 8, Section III), and the pairing of a superconductor's electrons from that push passed through the slow motion of the lattice (Chapter 9, Section

VI). I reason from this that what is new on the rung of gatherings is the number of wholes, and with it the counting of the ways they can share their energy.

That counting decides which arrangement a gathering takes. A gathering held at a fixed temperature settles where its free energy, its energy less its temperature times its entropy, is least (Chapter 2, Section XIV). The bonds and pulls of Volume One set the energy of each arrangement, the counting sets its entropy, and the temperature weighs the one against the other. So the same molecules of water are ice, water or steam according to the temperature and the pressure, along the lines of a map that the free energy draws (Chapter 4, Section V). The same iron is a magnet below 1043 kelvin and not above it (Chapter 8, Section V). And the same helium-4 is an ordinary liquid above 2.17 kelvin and a liquid that flows without friction below it (Chapter 9, Section V).

When a gathering is cold enough for its energy to win, it takes an order that belongs to the whole gathering and to none of its members. Three such orders carry this volume. A repeat of the atoms' places makes a crystal (Chapter 5, Section I). A direction picked by the spins and held by all of them makes a magnet (Chapter 8, Section IV). And one phase shared by very many wholes makes a superfluid or a superconductor (Chapter 9, Sections II and VIII). Each order belongs to the many: one atom has no repeat, one spin holds no direction against heat, and one helium atom has no shared phase. Each of these orders sets in sharply, at a point, because a symmetry or a jump separates the ordered arrangement from the disordered one. Where nothing separates two arrangements, the change between them is a crossover, a smooth change with no jump (Chapter 2, Section XV).

Gatherings also move in ways that no single whole moves. A *collective excitation* is a motion shared by many particles at once that comes in quanta: the phonons of a crystal (Chapter 5, Section IV), the holes of a nearly full band (Chapter 6, Section VII), the magnons of a magnet (Chapter 8, Section VI), and the excitations of fractional charge in the

quantum Hall states (Chapter 10, Section VIII). Each exists only while its gathering does, and none is a kind of particle: the closed list of the kinds is the same in a crystal of a billion billion atoms as in empty space.

And gatherings keep some numbers exactly. A phase shared by a whole ring of superconductor must come back to itself round the ring, so the ring holds magnetic flux only in whole units of $h/2e$ (Chapter 10, Section III). A sheet of electrons whose filled states carry a winding holds its Hall resistance at h/e^2 divided by a whole number (Chapter 10, Section VII). The whole numbers of Volume One, counted for one electron about one nucleus, are counted here by matter in bulk, to ten decimal places.

So we now know what is new when the wholes are many. The gatherings are held by the bonds and pulls of Volume One, with no new force and no new remainder. What is new is number, and with number the counting of ways, which with the temperature decides the arrangement. With it come the orders of the whole gathering, a repeat, a held direction and a shared phase, the collective excitations that move through it, and the whole numbers it keeps exactly.

V. The Two Rules on Every Rung

Two rules of the kinds have shaped every rung of both volumes. A *fermion* is a particle whose spin is an odd number of halves, such as the electron, and a *boson* is a particle whose spin is a whole number, such as the photon. The first rule is exclusion: by the principle of identity, two fermions of one kind in one state could not be told apart and so would be one, so no two share a state, while bosons crowd into one state freely. A whole of an odd number of fermions is excluded as a fermion is, while a whole of an even number is not (Chapter 1, Box 1.2; Volume One, Chapter 1, Box 1.2). The second rule is that angular momentum is counted in units of $\hbar$. It comes in whole units for motion along a path, because an angle about a

center closes after one turn, and in halves for a particle of spin one half, which returns only after two turns (Chapter 1, Box 1.3; Volume One, Chapter 7, Box 7.2).

In the wholes of Volume One, exclusion showed itself first as color. Three up quarks in their lowest state are found together, with their spins aligned, as the baryon called the Δ^{++}, and three alike fermions could not share that state, so they must differ in a further property: color, one of each (Volume One, Chapter 2, Box 2.2). Exclusion filled the shells of nuclei and of atoms, left no lasting nucleus of mass 5 or 8, gave the periodic table its periods, made each bond a pair of electrons of opposite spin, and made closed shells push apart. The counting of angular momentum in units sorted baryons, of spin 1/2 or 3/2, from mesons, of spin 0 or 1. With exclusion it let only the deuteron, of spin one, bind among pairs of nucleons. The pull binds a pair only with their spins aligned, and that arrangement is open only to a proton with a neutron, since two protons or two neutrons in one lowest state must take opposite spins (Volume One, Chapter 4, Box 4.3). It gave hydrogen its whole units of orbital angular momentum, and set the electron's magnet at one Bohr magneton (Volume One, Chapter 12, Section V).

In the gatherings of this volume, exclusion shows itself as the filling of states from the bottom. Fermions of one kind fill their states one to each up to a top, the Fermi-Dirac filling (Chapter 2, Section XII). Each band of a crystal holds two electrons for each cell of the repeat, one of each spin, so an odd count of electrons for each cell leaves a band partly filled and the solid conducts, while an even count can fill its bands and leave an insulator (Chapter 6, Sections IV and V). Exclusion, sorting the electrons' push by their spins, lines up iron's moments (Chapter 8, Section III). It lets two electrons just above a filled sea bind under any pull, because no state below them is free (Chapter 9, Section VII). And it holds up a white dwarf and a neutron star, whose fermions, crowded into their lowest states, press back with a pressure that needs no heat (Chapter 13, Section II), the same rule that stops a hand pressed on a table.

The other half of the first rule is that wholes of an even number of fermions are not excluded. Helium-4, six particles of spin one half, gathers into one state at 2.17 kelvin and flows without friction. Helium-3, five, cannot gather alone and waits for its atoms to pair, and the pairs of electrons in a superconductor, even wholes, share one phase (Chapter 9, Sections II, V and VIII). Photons are not excluded either, so a photon raises the probability that an excited atom gives out a photon into its own state, and light multiplies in a laser (Chapter 11, Section XIII). And the phonons of a crystal, not excluded, take any number to a mode (Chapter 5, Section IV).

The counting of angular momentum in units runs through this volume as whole numbers kept by matter. Round a superconducting ring the pairs' phase must come back to itself, so the flux through the ring comes in whole units of h/2e, the two being the pair's two units of charge (Chapter 10, Section III). Round a loop in a superfluid the flow comes in whole units of h/m (Chapter 9, Section IV). A nucleus of spin I has 2I + 1 orientations in a field, its angular momentum along the field running from $-I\hbar$ to $+I\hbar$ by ones, and taking up one photon changes it by one unit, which is how nuclear magnetic resonance works (Chapter 12, Section VII). And the halves show themselves too. A particle of spin one half reversed in time twice returns with its sign reversed, because it returns only after two full turns, so in a crystal that keeps time reversal the electrons' states come in partners of the same energy (Chapter 10, Section IX). That pairing gives the topological insulators their conducting surfaces, which nothing that keeps time reversal can remove (Chapter 10, Section IX).

So we now know that the two rules of Chapter 1 are the two rules of every rung, from the colors of three quarks to the pressure that holds up a neutron star. Exclusion fills states from the bottom and keeps fermions apart, while even wholes and photons gather. And angular momentum counts in whole units of $\hbar$ for every path and in halves for every spin one half, whether the turning is one electron's or that of a whole ring of metal.

VI. The Energies of the Ladder, and What They Make Possible

A chip works on a desk, a magnet on a refrigerator door, and water flows from a tap, all at room temperature. But the magnet of a hospital scanner must sit in liquid helium, and a reactor must split nuclei to draw on their energy, since no heat on Earth reaches into them. Why does each of these things work where it does?

Each rung of the ladder, and each order among many, has its own energy, and the gathering it lives in has a temperature. Chapter 2 found that in a gathering at temperature T the share of the ways that place an extra energy E in one part is $e^{-E/kT}$, the Boltzmann factor, where kT is the temperature as an energy. Chapter 3 found that a change needing an energy E goes at a rate in proportion to that share. So the one number that decides what heat can do to a binding or an order is its energy divided by kT. A binding many times kT is left alone by heat, and a binding of a few kT is broken and made again by heat all the time. A binding or a splitting far below kT is washed out, and is found only when the gathering is cooled until kT falls below it, or as a small excess of the lower of two levels. Box 14.1 sets the energies of both volumes against kT at room temperature.

Box 14.1. Each energy of the ladder against the temperature

Premises. (1) In a gathering at temperature T, the share of the ways that place an extra energy E in one part is $e^{-E/kT}$, and a change that needs E goes at a rate in proportion to that share (Chapter 2, Box 2.3; Chapter 3, Box 3.1). (2) The Boltzmann constant is $k = 8.617333262 \times 10^{-5}$ eV for each kelvin, exact since 2019, so at room temperature, 300 kelvin, kT = 0.0259 eV (Chapter 2, Section VIII). (3) The energies, each from the chapter that finds or measures it: a nucleon in a nucleus bound by up to about 8.8 MeV (Volume One, Chapter 4, Section VII); a chemical bond 1 to 10 eV, the hydrogen molecule's 4.48 eV (Volume One, Chapter 11, Section

XV); a photon of visible light 1.65 to 3.26 eV, wavelengths of 750 to 380 nanometers (Chapter 11, Section I); silicon's gap 1.12 eV (Chapter 6, Table 6.1); the hydrogen bond between two water molecules 0.137 eV (Volume One, Chapter 11, Section XIV, from Rocher-Casterline et al., 2011); iron's Curie point 1043 kelvin, at which kT is 0.090 eV (Chapter 8, Section V); a phosphorus atom's hold on its extra electron in silicon 0.045 eV (Chapter 7, Box 7.1); the cesium atom's hyperfine splitting, h times 9,192,631,770 hertz, 3.80×10^{-5} eV (Chapter 12, Section XV); aluminum's superconducting gap 0.18 thousandths of an eV, from its transition at 1.20 kelvin (Chapter 9, Section VIII); and the splitting of a proton's two orientations in a field of 1.5 tesla, 2.64×10^{-7} eV (Chapter 12, Section VII).

Steps. Divide each energy by kT = 0.0259 eV (computed). A nucleon's binding is 3.4×10^{8} kT. A bond's is 39 to 390 kT, the hydrogen molecule's 173 kT, so e^{-173} is about 10^{-75}. A visible photon carries 64 to 126 kT. Silicon's gap is 43 kT, and the number of electrons heat lifts across it goes as $e^{-E_g/2kT} = e^{-21.7} = 3.9 \times 10^{-10}$ (Chapter 6, Section VI). The hydrogen bond is 5.3 kT, and $e^{-5.3}$ is about 1/200. Iron's Curie point is 3.5 times room temperature. The donor's hold is 1.7 kT, and $e^{-1.7}$ is about 0.18. The cesium splitting is 0.0015 kT, aluminum's gap 0.007 kT, and the proton's splitting at 1.5 tesla 0.00001 kT.

Result. At room temperature heat leaves nuclei alone, their binding being hundreds of millions of times kT, and it leaves chemical bonds alone, the Boltzmann factor of even the weakest, at 39 kT, being about 10^{-17}. It lifts electrons across silicon's gap only in the share 3.9×10^{-10} that the factor $e^{-E_g/2kT}$ gives. It breaks and remakes hydrogen bonds all the time. It leaves iron aligned, since iron's Curie point lies well above room temperature, and it frees most donors' electrons. And it washes out a superconductor's gap and the finest splittings of atoms and nuclei: a gap is found only when the gathering is cooled below its transition, and a splitting at room temperature only as a small excess, a share of about E/2kT, in the lower of its two levels.

Every technology of this volume lives at one of these ratios, and Table 14.1 sets them side by side.

Table 14.1. The energies of the ladder against kT at room temperature, 0.0259 eV, with what each ratio gives and a technology that rests on it. The energies are those of Box 14.1, premise (3), with the chapters named there.

Energy	**Size**	**Against kT at 300 K**	**What follows at room temperature**	**At work**
Binding of a nucleon in a nucleus	up to about 8.8 MeV	3.4×10^8	nuclei untouched by heat and chemistry; their energy reached only by fission or by fusion through tunneling in a star's core	reactors; radiometric dating; the hospital's gamma-ray camera
Chemical bond	1 to 10 eV	39 to 390	molecules last; burning a fuel gives a few electron volts for each molecule, a millionth of a nuclear change	fuels and batteries; sunburn from ultraviolet photons that reach a bond's energy
Gap of silicon	1.12 eV	43	heat lifts few electrons across, so the carriers can be set by doping; light above the gap is taken up	chips; solar cells; camera sensors; light-emitting diodes (LEDs), whose color is their gap
Hydrogen bond between water molecules	0.137 eV	5.3	broken and remade by heat all the time, so water flows, yet strong enough to hold it liquid far above	water; the two strands of deoxyribonucleic acid (DNA), the molecule of inher-

			the boiling points of its heavier neighbors	itance, held together and yet parted to be copied
Magnetic order of iron (kT at its Curie point)	0.090 eV	3.5	iron stays aligned below 1043 kelvin	motors, generators, hard drives
Hold of a donor in silicon	0.045 eV	1.7	almost every donor gives its electron to the band	every n-type region of a chip
Hyperfine splitting of cesium	3.80×10^{-5} eV	0.0015	the two levels nearly equally filled, read by microwaves of one frequency	the second, and the clocks of satellite navigation
Gap of a superconductor (aluminum)	0.18 thousandths of an eV	0.007	washed out by heat; pairs form only when cooled below the transition	scanners' magnets in liquid helium; the volt from Josephson junctions
Splitting of a proton's orientations at 1.5 tesla	2.64×10^{-7} eV	0.00001	an excess of a few in a million in the lower orientation, enough for a signal	magnetic resonance imaging; nuclear magnetic resonance in chemistry

Read down the table, and the reasons for the world's machines appear. A reactor draws on nuclei, and a fire on bonds. A kilogram of uranium-235 split gives about half a million times the energy of a kilogram of hydrogen burned, and a kilogram of hydrogen fused about four and a half million times the energy of the same kilogram burned. The reason is that a nucleon's binding is about a million times a bond's, to within a factor of a few (Volume One, Chapter 4, In Use, and Chapter 12, Box 12.1). A chip works at room temperature because two of its energies stand on either

side of kT. Silicon's gap, 43 kT, keeps heat from setting its carriers, and the donor's hold, 1.7 kT, lets heat free nearly every carrier that the maker puts in, 99.6 percent of them at the doping of Chapter 7 (Chapter 7, Section II). An LED and a solar cell work because a semiconductor's gap lies near the energy of a photon of light, so the gap can be chosen for the color to be given out or the sunlight to be taken in (Chapter 7, Sections VI and VII). Water is liquid at room temperature, where its heavier neighbors hydrogen sulfide, selenide and telluride are gases, because its hydrogen bonds stand a few kT above the jostling of heat. Water's hydrogen bonds are strong enough to keep the molecules touching and too weak to fix the molecules in place, so the molecules change neighbors and the water flows (Chapter 4, Sections IV and VI). Iron holds a magnetic direction at room temperature because its Curie point, 1043 kelvin, is three and a half times room temperature, and a nail heated red-hot loses its hold on a magnet (Chapter 8, Sections I and V). And the superconducting magnet of a scanner sits in liquid helium because the order it rests on, a gap of tenths of a thousandth to about a thousandth of an electron volt (aluminum's 0.18 and lead's 1.09 thousandths, Chapter 9, Section VIII), is washed out by the heat of a room. The cuprate tapes of Chapter 9, In Use, work at the 77 kelvin of liquid nitrogen because their transition lies above it.

So we now know what the energies make possible. Each binding works where its energy stands well above kT, and each order among many appears only where kT falls below its energy. The ratio of the two, read from the Boltzmann factor, decides which machines work at room temperature and which must be cooled.

VII. Where Structure Ends and History Begins

Cut two bars from one piece of steel and heat both red-hot. Plunge the first into cold water and let the second cool slowly. Their atoms are the same atoms, of iron with a little carbon, held by the same bonds, and yet the first comes out hard and brittle and the second much softer (Chapter 5, In Use). The difference lies in what was done to each.

Volume One asked three questions of every rung, each with its own kind of answer: which wholes exist is structure, which last is structure and measured values, and how many there are is history (Volume One, Chapter 1, Section VI, and Chapter 12, Section VI). The gatherings of this volume answer the same three, and they show more sharply where each kind of answer begins.

Structure fixes the whole numbers that matter keeps. A repeat can be turned onto itself only by a half, a third, a quarter or a sixth of a turn, so crystals come in 14 kinds of lattice and 230 space groups, the same in every crystal anywhere (Chapter 5, Section III). Each band holds two electrons for each cell, so an odd count of electrons for each cell leaves a band partly filled (Chapter 6, Section V). The pair that carries a superconductor's current has two units of charge, and the phase round a ring comes back after a whole number of turns, so the flux comes in whole units of $h/2e$. The Hall conductance is a winding, so it is a whole number of units of e^2/h (Chapter 10, Section X). A nucleus of spin I has $2I + 1$ orientations, and a white dwarf's greatest mass is built of $\hbar$, c, the constant of gravitation and the nucleon's mass in a form that structure fixes (Chapter 12, Section VII; Chapter 13, Box 13.2). These whole numbers are the same in every material, and Chapter 10, Section X, says it in one sentence: the Planck constant and the electron's charge are values, and the factors by which they enter, the two of the pair and the whole numbers, are fixed by structure.

Measured values fix which of the allowed cases each substance is, and where. They set whether a solid is a metal or an insulator and how wide its gap is, whether a crystal's spins line up, alternate or stay unaligned and at what temperature that order is lost, at what temperature a metal's electrons pair, and how strongly glass slows light. The values that set them are those of the atoms: the overlap of their states, the strength of their push and the masses of their parts (Chapter 6, Summary; Chapter 8, Section III; Chapter 9, Section XIII; Chapter 11, Summary). The structure that sorts them, the free energy, exclusion and angular momentum in whole and half units, is the same for all.

History enters the gatherings in two ways. The first way that history enters is the way Volume One found: how many of each kind of atom there are. The first minutes of the universe left hydrogen and helium-4, and the stars made carbon, oxygen and iron. The nuclei beyond iron were built where neutrons were taken in, some of them in the mergers of neutron stars (Volume One, Chapter 6; Chapter 13, In Use). Structure permits gold, and how much gold the Earth holds is set by where and how often its nuclei were made.

The second way is new to this volume: which of its allowed states a piece of matter is found in, when it has not reached its balance. A gathering left long enough at one temperature settles in its state of least free energy, and then its state is structure and values alone. A gathering that has not had that time keeps a trace of what was done to it. A glass is a liquid cooled too fast to find its rows, and the temperature at which it stops flowing shifts with how fast it was cooled (Chapter 4, Section VII). A crystal cooled too fast to settle into its single ground state keeps a residual entropy, the count of the arrangements it was caught among (Chapter 2, Section XVI). A magnet keeps the direction the last strong field gave it, its remanence, because the walls between its domains catch on flaws, and that memory of a field is how a hard drive holds a bit (Chapter 8, Section VII and In Use). And the quenched bar of steel is hard because the sudden cooling left its lattice strained, with no time to give back the carbon it had taken into its gaps when hot (Chapter 5, In Use). In each of these, the

bonds and the counting say which states are possible, the measured values say which state is least, and the history of the piece says which state it is in.

So we now know where structure ends and history begins. Structure fixes the whole numbers that matter keeps and the kinds of order, the same in every material. Measured values fix which case each substance is and where its changes fall. And history fixes how much of each element there is, and, wherever a gathering has not reached its balance, which of its allowed states it keeps.

VIII. The Kinds and What They Make

In *The Coming of the Kinds*, which these two volumes continue, I asked how all the particles came to be, and I answered in three parts. I gave the first two in these words: "The kinds are given by structure. Their presence was made by the cooling, kind by kind, in order of falling temperature" (*The Coming of the Kinds*, Chapter 14, Section VI). I gave the third part in the same section's words: "The amount of matter is a residue the turn leaves, kept by every change after it, and the kinds fix the share of that residue held as baryons". The turn is that book's name for "the limit that our history, traced backward, takes for its beginning", and a residue is "what remains when nearly everything else has gone one way" (*The Coming of the Kinds*, Preface). That book ended where the first atoms formed, about 370,000 years into our history, with hydrogen and helium, an electron for each proton, the light set free and the sea of neutrinos.

In these two volumes I take up what those few kinds make. The answer I give has four parts.

The first of the four parts is that the kinds are few and the wholes are without number. Ordinary matter uses three kinds of particle of matter, the up quark, the down quark and the electron, held by photons and gluons. From them come every nucleus, every atom of the periodic table, every molecule, and every gas, liquid, crystal, metal, semiconductor, mag-

net, superfluid and star of this volume. *The Story of the Particles* states the lesson at its first bound whole, the atom: "The building blocks are few. The combinations are inexhaustible" and "Richness does not require a proliferation of kinds. It requires a small number of kinds with a rich combinatorics" (*The Story of the Particles*, Level 1, Section II). The phonons, holes, magnons and excitations of fractional charge of the gatherings are motions of many members at once, so the closed list of the kinds stands as it was, the same in both volumes.

The second part is the shape of what the kinds make: a ladder of levels, each held by what the level below leaves over and each held far more weakly than the level below. It runs from the confined color field that makes nearly all of a proton's mass to the hydrogen bond that keeps water liquid (Sections II and III). On the rung of gatherings no further remainder of a force appears. What is new is number, with the counting of ways that decides which arrangement very many wholes take at each temperature, and the orders of the whole gathering that set in when it is cold (Section IV).

The third of the four parts is that two rules of the kinds shape every rung. Exclusion comes from the principle of identity, and angular momentum in whole and half units of ħ comes from an angle that closes after one turn and a spin one half that returns only after two. Together they sort every whole into those excluded and those not, fill every shell and every band, stop every hand pressed on a table, hold up every white dwarf, gather the even wholes of a superfluid into one state, and count the flux of a superconducting ring (Section V).

The fourth is the division of every answer into structure, values and history. Which wholes and which orders can exist, and the whole numbers they keep, are structure, the same everywhere and at every moment. Which of them last, and where each substance falls among the cases structure allows, are set by measured values. How much of each there is, and which allowed state a particular piece of matter has been left in, are history (Sections VI and VII).

Read with *The Coming of the Kinds*, the account of these two volumes runs whole. The kinds are given by structure, their presence was made by the cooling, and the amount of matter is a residue the turn leaves. What the kinds make, once the universe is cool enough for wholes to hold, is the ladder of these two volumes. Each rung is held by what the one below leaves over, shaped on every rung by exclusion and by angular momentum in whole and half units, and settled, where the wholes are many, by the counting of ways.

In Use

Take the telephone of Section I apart, rung by rung, and every chapter of the two volumes is found at work in it.

Its connectors are plated with gold, because gold does not tarnish (Volume One, Chapter 10, In Use). Gold's yellow color and its hold on its outer electron, the firmest of any metal of its column, both come from the speed of its innermost electrons, more than half the speed of light, which draws its outer s state in (Volume One, Chapter 10, Sections V and VIII, and In Use). And the gold itself was made in a star or where two neutron stars merged, its nuclei built by taking in neutrons (Volume One, Chapter 6; Chapter 13, In Use). How much of it the Earth holds is history.

Its battery is a lithium-ion cell of 3.6 or 3.7 volts, lithium giving up the one outer electron that sits outside its closed core (Chapter 1, In Use; Chapter 3, In Use). Its energy is chemical, a few electron volts for each atom, about a millionth of what a nuclear change would give.

Its chip is a crystal of silicon, whose atoms repeat because atoms of one kind differ only by where they are (Chapter 5, Section I). Its gap of 1.12 eV, 43 times kT, lets heat set almost none of its carriers (Chapter 6, Section VI), and how many heat does set is the counting of ways of Chapter 2, through the Boltzmann factor (Chapter 2, Section X). Phosphorus and boron are set into it on purpose, each binding its extra electron, or its missing one, by a few hundredths of an electron volt, so that

heat frees nearly all of them (Chapter 7, Section II and Box 7.1). Its billions of transistors are junctions whose barriers a gate's voltage raises and lowers (Chapter 7, Sections III to V), and its wiring is copper, whose odd count of electrons for each atom leaves a band half filled (Chapter 6, In Use). Its camera is a sheet of photodiodes that turn light above the gap into current (Chapter 7, In Use).

Its screen is glass that bends and passes light because the light's phase falls behind as it drives the glass's electrons, every part of it traveling at c (Chapter 11, Section III). A coating of indium tin oxide, whose gap is wider than any photon of visible light and whose tin atoms give it free electrons, conducts across the screen and lets the light through (Chapter 6, In Use). And a liquid-crystal display, where it has one, sets each small region light or dark by turning the rods of a nematic liquid, which shares a direction while it flows, between two polarizers (Chapter 4, In Use; Chapter 11, Section VIII).

Its sense of place comes from the clocks of navigation satellites, atomic clocks whose frequency is the same for every atom of one kind because such atoms cannot be told apart. Those clocks are set to run slow by about 38 microseconds a day, to undo the shift that gravitation and the satellites' motion make (Chapter 12, In Use, after Ashby, 2003). Its calls cross the world as light held in glass fibers by total internal reflection (Chapter 11, In Use).

And the volts of its battery and its chip are measured against a standard kept by superconductors. National laboratories keep the volt with arrays of Josephson junctions, made of the superconducting metals of Chapter 9 and cooled in liquid helium, whose voltages depend on nothing but a frequency and the exact ratio 2e/h (Chapter 9, Section VIII; Chapter 10, In Use). A calibrated meter that checks the telephone's cell traces its reading back to them (Chapter 10, In Use).

And beneath every one of these lies the first rung. The atoms of its glass, its silicon and its gold weigh what they weigh because nearly all of a proton's mass is the energy of the confined color field. They last because

the proton is the lightest baryon and the neutron, heavier, lasts inside the nuclei of stable atoms (Volume One, Chapters 2, 3 and 5). A telephone is the whole ladder, held in one hand.

Summary

The two volumes of *The Matter We Know* climb one ladder. Volume One found the wholes one at a time. Quarks are held by the confined color field into protons and neutrons, and nucleons by its colorless leftover, reaching about 1.4 fm, into nuclei that last when nothing lighter carries their counts. Electrons are held by the nucleus's whole charge into atoms, whose size is the balance of the cost of confinement against the electric pull and whose subshells fill into the periods and families of the periodic table. And atoms are held by their outer electrons into molecules, by bonds of 1 to 10 eV, each a fraction of the Rydberg energy, 13.6 eV. This volume found what very many wholes do together. It found the counting of ways that gives temperature and entropy and decides where every change settles, the phases of matter, the repeat of crystals, and the bands that make metals, insulators and semiconductors, with the devices built from them. It found the held direction of a magnet, the one phase of a superfluid and a superconductor, and the whole numbers that matter counts exactly. And it found the slowing of light as a sum of waves each at c, the places where the nucleus shows through, and the exclusion that holds up a white dwarf and a neutron star.

On every rung of the wholes, each level is held by what the level below leaves over and far more weakly than the one below. On the rung of gatherings no further remainder of a force appears: the gatherings are held by the bonds of Volume One and the feeble pulls between molecules. What is new is the number of wholes, with the counting of ways that decides, at each temperature, which arrangement they take. With it come the orders

that belong to the whole gathering, a repeat, a held direction and a shared phase, each setting in at a point where a symmetry or a jump separates it from disorder.

Two rules of the kinds shape every rung of both volumes. Exclusion, from the principle of identity, fills states from the bottom, makes bonds pairs and holds up stars, while even wholes and photons gather into one state. Angular momentum comes in whole units of ħ for a path and in halves for spin one half, which gives the shells, the spins of nuclei, and the whole numbers of flux and conductance that matter keeps. The energy of each rung and each order, set against kT, the temperature as an energy, decides what heat does to it. Nuclei and bonds are left alone at room temperature, hydrogen bonds and a donor's hold are broken by heat, iron's order holds, and superconductors and the finest splittings are found only by cooling. That one ratio says which machines work in a room and which must be cooled (Box 14.1, Table 14.1).

Structure fixes the whole numbers that matter keeps and the kinds of order, the same in every material and at every moment. Measured values fix which case each substance is and where its changes fall. And history fixes how much of each element there is and, where a gathering has not reached its balance, which of its allowed states it keeps. With *The Coming of the Kinds* the two volumes make one account. The kinds are given by structure, their presence was made by the cooling, and the amount of matter is a residue the turn leaves. What the kinds make is this ladder of wholes and of their gatherings, from the proton to the solid in a hand and the star in the sky.

✶

KEY CONCEPTS

- **The ladder of levels.** Matter built in levels, quarks into nucleons, nucleons into nuclei, nuclei and electrons into atoms, atoms into molecules, molecules into larger gatherings, each held by what the level below leaves over and each far more weakly than the one below.

- **Tunneling.** A particle's crossing of a barrier with less energy than the barrier, because its wave extends past the region in which it is confined.
- **Entropy; temperature.** The logarithm of the number of a system's microstates with its totals; the energy it takes to raise a system's entropy by one unit.
- **Boltzmann factor; kT.** $e^{-E/kT}$, the share of the ways that place an extra energy E in one part of a gathering at temperature T; kT, the temperature as an energy, 0.0259 eV at 300 kelvin.
- **Crystal; band.** A solid whose atoms stand in one arrangement repeated through space; the set of electron states in a crystal that grow from one state of the single atom.
- **Spontaneous symmetry breaking; crossover.** A symmetry of the laws that the state of least energy does not share; a smooth change with no jump, found where nothing separates two arrangements.
- **Condensate.** A gathering of many wholes into one state, with one amplitude and one phase across the whole of it.
- **Collective excitation.** A motion shared by many particles at once that comes in quanta, such as a phonon, a hole or a magnon; it exists only while its gathering does and is not a kind of particle.
- **Refractive index.** The ratio n of the speed of light c to the speed at which the phase of light advances in a material.
- **Fermion and boson.** A particle whose spin is an odd number of halves; a particle whose spin is a whole number.
- **The two rules of the kinds.** Exclusion, by which no two fermions of one kind share a state and a whole of an odd number of fermions is excluded while one of an even number is not; and angular momentum in whole units of ħ for a path and in halves for spin one half.
- **What is new when the wholes are many.** No new force: gatherings are held by the bonds of single wholes and the feeble pulls between molecules, and their arrangement is decided by the counting of ways at

each temperature, with orders of the whole gathering (a repeat, a held direction, a shared phase), collective excitations, and whole numbers kept exactly.

- **Energy against kT.** The ratio that decides what heat does to a binding or an order: far above one, heat leaves it alone; a few, heat breaks and remakes it; far below one, it is found only by cooling (Box 14.1).
- **Structure, values and history.** Which wholes and orders exist, and the whole numbers they keep, are structure; which last, and where each substance falls, are measured values; how much of each there is, and which allowed state a piece of matter that has not reached its balance keeps, are history.

The Measured Values Used in This Volume

The table gives every measured value the volume uses, with its source, and with its uncertainty wherever the source states one. An uncertainty is written either after $\pm$ or in parentheses, where the figures in parentheses are the uncertainty in the last digits of the value: 0.84075(64) fm means 0.84075 ± 0.00064 fm. A value marked exact is fixed by the definition of the units, and a value marked computed is worked out from measured values by the chapter or box named. The values derived from these stand in the boxes that derive them. Each source is named in short, and the Bibliography gives it in full: CODATA 2022 is the set of values recommended in 2022 by the Committee on Data of the International Science Council (Mohr et al., 2025); PDG is the Particle Data Group (Navas et al., 2024; Takahashi et al., 2026); NIST is the National Institute of Standards and Technology, whose table of atomic masses is the source of every atomic mass below; IAPWS is the International Association for the Properties of Water and Steam. A source named as standard tables or standard accounts is the common reference value of its field, as the chapter that uses it says. The last column gives the chapters of this volume that use each value; Preface is the Preface, and Brief is The Ladder in Brief with its notes.

Quantity	Value	Source	Chapters
Constants and units			
Speed of light, c	299,792,458 m/s (exact)	the definition of the meter	1, 11
Planck constant, h	$6.62607015 \times 10^{-34}$ J s (exact since 20 May 2019)	International Bureau of Weights and Measures (2019)	2, 10
Reduced Planck constant, ħ	$1.054571817... \times 10^{-34}$ J s (exact)	CODATA 2022	1, 6
ħc	197.3269804... MeV fm (exact)	CODATA 2022	1, Brief
Elementary charge, e			3, 10

Quantity	Value	Source	Chapters
	$1.602176634 \times 10^{-19}$ C (exact since 20 May 2019)	International Bureau of Weights and Measures (2019)	
Boltzmann constant, k	1.380649×10^{-23} J/K, $8.617333262... \times 10^{-5}$ eV per kelvin (exact since 2019)	CODATA 2022	2 to 14, Brief
Avogadro constant, N_A	$6.02214076 \times 10^{23}$ per mole (exact)	CODATA 2022	2, 3, 6
Gas constant, $R = N_A k$	8.314462618... J per kelvin and mole (exact, computed)	from k and N_A	3, 4
Faraday constant, $F = N_A e$	96,485.33212... C per mole (exact, computed)	from e and N_A	3
Fine-structure constant, α	1/137.035999177(21)	CODATA 2022	1, 10, 11
Newton's constant, G	$6.67430(15) \times 10^{-11}$ m^3 kg^{-1} s^{-2}	CODATA 2022	13
Atomic mass unit	$1.66053906892(52) \times 10^{-27}$ kg; 931.49410372(29) MeV	CODATA 2022	2, 4, 12, 13
Electron mass	$9.1093837139(28) \times 10^{-31}$ kg	CODATA 2022	6
Stefan-Boltzmann constant, σ	$5.670374419... \times 10^{-8}$ W m^{-2} K^{-4} (exact)	CODATA 2022	2
Wien's constant, b	$2.897771955... \times 10^{-3}$ m K (exact)	CODATA 2022	2
Bohr magneton, μ_B	$9.2740100657(29) \times 10^{-24}$ J/T	CODATA 2022	8, 12
Nuclear magneton, μ_N	$5.0507837393(16) \times 10^{-27}$ J/T	CODATA 2022	12
Magnetic constant, μ_0	$1.25663706127(20) \times 10^{-6}$ N/A^2	CODATA 2022	8, 9, 10
Impedance of empty space, $Z_0 = \mu_0 c$	376.730313412(59) Ω	CODATA 2022	10
Flux quantum, h/2e	$2.067833848... \times 10^{-15}$ Wb (exact)	CODATA 2022	9, 10
Josephson constant, 2e/h; von Klitzing constant, h/e^2	483,597.8484... GHz/V; 25,812.80745... Ω (both exact, computed)	from h and e	10
Cesium-133 hyperfine frequency	9,192,631,770 Hz (exact; the definition of the second)	International Bureau of Weights and Measures, the definition of the second	12, 14

Quantity	Value	Source	Chapters
Standard atmosphere; bar	101,325 Pa; 100,000 Pa (both exact, by definition)	the definitions of the units	2, 3, 4
Masses of a water molecule, a nitrogen molecule, and one sodium and one chlorine atom together; atomic weights of iron and copper	18.015; 28.014; 58.443 atomic mass units; 55.845; 63.546	standard atomic weights	2, 4, 5, 6, 8
The kinds of particle			
Up and down quark masses, at 2 GeV	2.16 ± 0.07 MeV; 4.70 ± 0.07 MeV	PDG 2024, as Volume One, Table 1.1, gives them	1
Electron mass, $m_e c^2$	0.51099895069(16) MeV	CODATA 2022	1
Heaviest neutrino's mass	at least 0.0502 ± 0.0002 eV (about 0.05 eV)	PDG 2026, as Volume One, Table 1.1, gives it	1
W boson mass	80.3625 ± 0.0077 GeV	PDG 2026	1
Z boson mass	91.1880 ± 0.0020 GeV	PDG 2024	1
Higgs boson mass; endpoint of a settling with a jump	125.13 ± 0.11 GeV; near 72 GeV	*The Coming of the Kinds*, Chapter 4, Section IV	8
Charged pion mass	139.57039(17) MeV	PDG 2026	1, Brief
Proton mass	938.27208943(29) MeV	CODATA 2022	1, Brief
Neutron mass	939.56542194(48) MeV	CODATA 2022	1
Neutron less proton mass	1.29333251(38) MeV (1.293 MeV)	CODATA 2022	1
Free neutron mean life, average	878.3 ± 0.4 s	PDG 2026 (the Particle Data Group's average)	1, 13, 14
Nucleon mass, lattice computation	936 ± 25 ± 22 MeV	Dürr et al. (2008)	Brief
Proton charge radius	0.84075(64) fm	CODATA 2022	1, Brief
Magnetic moments of the proton, the neutron and the deuteron	2.79284734463(82); −1.91304276(45); 0.8574382335(22) nuclear magnetons	CODATA 2022	1, 12
Proton gyromagnetic ratio over 2π	42.577478461(18) MHz per tesla	CODATA 2022	12, 14
Nuclei			

Quantity	Value	Source	Chapters
Nuclear radius; central density	about 1.2 $A^{1/3}$ fm; about 0.16 nucleons per cubic femtometer	Krane (1987), as Volume One, Chapter 4, Section VI, gives it	1, 13, Brief
Deuteron binding energy	2.2246 MeV (2.224566 MeV, computed)	CODATA 2022 masses, as Volume One, Chapter 4, Section VIII, gives it	Brief
Helium-4 nucleus, binding energy	28.30 MeV (computed)	NIST atomic masses, as Volume One, Chapter 4, Section VIII, gives it	1
Atomic masses of iron-56 and nickel-62	55.93493633(49) u; 61.92834537(55) u	NIST	Brief
Binding for each nucleon at the top of the curve	about 8.8 MeV, near iron-56 and nickel-62 (8.790 and 8.795 MeV, computed)	NIST atomic masses, as Volume One, Chapter 4, Section VII, gives it	1, 14, Brief
Stable nuclides	251	the stable-nuclide listings, as Volume One, Chapter 5, Section I, gives it	1
Atomic masses of helium-4 and helium-3	4.00260325413(6) u; 3.0160293201(25) u	NIST	9
Iron-57: gamma ray of its first excited state; mass; mean life of the state	14.4125 keV; 56.935 u; about 141 ns (natural width 4.7×10^{-9} eV, computed)	standard tables of nuclides	12
Nuclear spins: deuterium; nitrogen-14; boron-10	1; 1; 3	standard tables of nuclear spins	12
Gyromagnetic ratios over 2π: hydrogen-2, carbon-13, nitrogen-14, nitrogen-15, oxygen-17, fluorine-19, phosphorus-31, iron-57	6.536; 10.708; 3.077; −4.316; −5.772; 40.078; 17.235; 1.382 MHz per tesla	standard tables	12
Natural shares: hydrogen-1, hydrogen-2, carbon-12, carbon-13, nitrogen-14, nitrogen-15, oxygen-16, oxygen-17, fluorine-19, phosphorus-31, iron-57	99.98; 0.016; 98.9; 1.1; 99.6; 0.4; 99.76; 0.04; 100; 100; 2.1 percent	standard tables of nuclides	12
Deuterium in ocean water	156 hydrogen atoms in each million, about one in 6,400	standard tables of the abundance of deuterium	12

Quantity	Value	Source	Chapters
Beryllium-7 half-life, inside a cage of sixty carbon atoms; in beryllium metal	52.68 ± 0.05 days; 53.12 ± 0.05 days	Ohtsuki et al. (2004)	12
Dysprosium-163 stripped of its electrons, half-life	47 ± 5 days	Jung et al. (1992)	12
Rhenium-187 half-life, neutral atom; fully stripped	about 4.1×10^{10} years; 32.9 years	Bosch et al. (1996)	12
Technetium-99m decay rates in potassium pertechnetate and technetium sulfide	differ by 0.27 percent	Bainbridge, Goldhaber and Wilson (1953)	12
The first atoms, the early universe and the Sun			
Last scattering of the early light	2,973 kelvin, about 370,000 years	*The Coming of the Kinds*, Chapter 13	Preface, 2
Helium-4's share of the mass of ordinary matter, from the first minutes	about a quarter (0.245 ± 0.003)	PDG 2026, as *The Coming of the Kinds*, Chapter 12, gives it	1
Photons for each hydrogen nucleus; half of hydrogen's electrons bound in balance	2.2 billion; near 3,700 kelvin, 0.32 eV	*The Coming of the Kinds*, Box 13.1	2
Temperature of the cosmic microwave background	2.72548 ± 0.00057 K	Fixsen (2009)	2
Departure of the background's spectrum from a black body	less than 50 parts in a million of the peak	Fixsen et al. (1996)	2
Photons of the background	411 in each cubic centimeter	*The Coming of the Kinds*, Box 1.1	2
The Higgs field's crossover; the quarks' crossover	centered at 159.5 ± 1.5 GeV; near 156.5 ± 1.5 MeV	*The Coming of the Kinds*, Chapters 4, 6 and 8	2
Temperature of the Sun's surface	5772 K (nominal); 5772.0 ± 0.8 K	International Astronomical Union (2015); Prša et al. (2016)	2, 11
Atoms and molecules			
First ionization energies: hydrogen, helium, lithium, neon, sodium, cesium (eV)	H 13.598434599702(12); He 24.587389011(25); Li 5.391714996(22); Ne 21.564541(7); Na 5.13907696(25); Cs 3.89390572743(17)	Kramida et al. (2024)	1, 2, Brief

Quantity	Value	Source	Chapters
Electron affinity of chlorine	3.612725(28) eV	Andersen, Haugen and Hotop (1999)	1
K-shell binding energy of barium	37,441 eV	Thompson et al. (2009), Table 1-1	Brief
Ionic radius of Cs^+ among eight neighbors	174 pm	Shannon (1976)	Brief
Energy to separate H_2 into its atoms, D_0	36,118.06962(37) per centimeter, 4.4781 eV	Liu et al. (2009)	1, 12, 14, Brief
Energy to separate D_2 into its atoms, D_0	36,748.36286(68) per centimeter, 4.5562 eV	Liu et al. (2010), as Volume One, Chapter 11, Section XVI, gives it	12
Bond lengths: H_2; Li_2	74.1 pm; 267.3 pm	Johnson (2022)	1, Brief
Energies to separate molecules into their atoms: Li_2; N_2; HCl	1.0 eV; 9.80 eV (945.41 kJ per mole); 4.4 eV	Huber and Herzberg (1979); for N_2, Greenwood and Earnshaw (1997)	1, Brief
Lattice energy of salt, NaCl	7.94 eV for each pair of ions	Kittel (2005)	1, Brief
Energies to take a metal apart into atoms: sodium; tungsten	1.113; 8.90 eV for each atom	Kittel (2005)	1, Brief
Energy to separate two water molecules held by a hydrogen bond	1105 ± 10 per centimeter, 0.137 eV	Rocher-Casterline et al. (2011)	1, 14, Brief
Helium pair: binding	1.1 $(+0.3, -0.2)$ thousandths of a kelvin, times k (about 10^{-7} eV)	Grisenti et al. (2000)	1, Brief
Stretching vibrations of bonds of carbon to hydrogen and to deuterium	about 2,900 and 2,100 per centimeter	standard infrared spectroscopy	3
Counting, gases and phases			
Bose-Einstein condensate of rubidium-87	first appeared near 170 nK, on 5 June 1995	Anderson et al. (1995)	2, 9
Hard spheres: largest share of space for the disordered arrangement; least for the crystal	49.4 percent; 54.5 percent	Hoover and Ree (1968), as Pusey et al. (2009) give them	2
Helium-3: the solid's entropy above the liquid's	below about 0.3 K		2

Quantity	Value	Source	Chapters
		the effect Pomeranchuk (1950) predicted, as Chapter 2, Section XIV, gives it	
Residual entropy of ice	0.82 $\pm$ 0.05 calories for each kelvin and mole, 3.4 $\pm$ 0.2 J per kelvin and mole	Giauque and Stout (1936)	2
Heat taken up at 25 degrees Celsius by a mole: liquid water; liquid ethanol	75.3 J for each kelvin (4.18 J for each gram); 112.4 J for each kelvin (2.44 J for each gram)	Chase (1998); Petrov et al. (1989); as the NIST Chemistry WebBook gives them	2
Curie point of iron	1043 K (770 degrees Celsius)	standard tables of magnetic materials	2, 8, 9, 14, Brief
Critical point of water	647.096 K; 22.064 MPa	Wagner and Pruß (2002); IAPWS (1992)	2, 4
Triple point of water	273.16 K; 611.657 Pa	IAPWS (2008)	4
Water at 101,325 Pa: melting point; boiling point	273.15 K; 373.12 K (computed from the IAPWS equations)	IAPWS (1992, 2008)	4
Melting curve of ordinary ice: its end, where other forms of ice take over	208.566 MPa at 251.165 K	IAPWS (2008)	4
Surface tension of water at 25 degrees Celsius	71.97 thousandths of a joule for each square meter	IAPWS (2014)	4
Latent heat of melting ice; of boiling water at its normal boiling point	333.55 kJ for each kilogram (6.01 kJ for each mole); 40.65 kJ for each mole	CRC Handbook of Chemistry and Physics, 62nd edition (1981)	4
Density of water: at 25 degrees Celsius; at 0 degrees Celsius; at its greatest, near 4 degrees Celsius	997.05; 999.84; 999.97 kg per cubic meter	Engineering ToolBox; CRC Handbook, 97th edition (Harvey, 2017); Engineering ToolBox	4
Density of ice at 0 degrees Celsius	916.7 kg per cubic meter	CRC Handbook, 97th edition (Harvey, 2017)	4
Distance between neighboring oxygen atoms in ice	0.276 nm	Petrenko and Whitworth (1999)	4
Boiling points of H_2S, H_2Se, H_2Te	-60.3; -41.3; -4 degrees Celsius	Greenwood and Earnshaw (1997)	4
Critical point of carbon dioxide	304.1282 K; 7.377298 MPa; 94.12 cubic centimeters for each mole	Span and Wagner (1996)	4

Quantity	Value	Source	Chapters
Critical temperature of carbon dioxide, as Andrews found it	near 31 degrees Celsius	Andrews (1869)	4
Triple point of carbon dioxide	216.592 K; 517,964 Pa	Span and Wagner (1996)	4
Butane: boiling point at the pressure of the air; pressure of its vapor at 25 degrees Celsius	273 ± 1 K; about 2.4 bar (computed)	NIST Chemistry WebBook; Das, Reed and Eubank (1973), as the WebBook fits them	4
Viscosity of a solid glass	at least 10^{12} to 10^{13} pascal seconds	Zanotto (1998)	4
Glass transition of flat soda-lime glass	near 564 degrees Celsius	Seward and Vascott (2005)	4
Glass transition of polyethylene terephthalate	70 to 85 degrees Celsius	NETZSCH, polymer database	4
Cholesteryl benzoate: melts into a cloudy liquid; turns clear	145.5 degrees Celsius; 178.5 degrees Celsius	Reinitzer (1888)	4
Size of colloidal particles	roughly a billionth to a millionth of a meter	the range of the International Union of Pure and Applied Chemistry	4
Concentration above which sodium dodecyl sulfate forms micelles, 25 degrees Celsius	about 0.008 moles in each liter	Mukerjee and Mysels (1971)	4
Free electrons of the upper atmosphere at its densest	about 10^{12} in each cubic meter	German Aerospace Center, Ionosphere Monitoring and Prediction Center	4
Fluorescent lamp: ultraviolet lines of mercury; their share of the energy put in	253.7 and 185.1 nm; about 63 percent	Lamptech, "Fluorescent Lamp Operation"	4
Temperature that the plasma of ITER must reach	150 million degrees Celsius	ITER Organization	4
Reactions and cells			
Rise of a reaction's rate for each one-degree rise at ordinary temperatures, in the reaction Arrhenius studied	10 to 15 percent	Arrhenius (1889)	3

Quantity	Value	Source	Chapters
Hydroxymethylene becoming formaldehyde by tunneling, in argon at 11 kelvin	half-life about 2 hours	Schreiner et al. (2008)	3
Orotidine 5′-monophosphate losing carbon dioxide: half-time with the enzyme; in water without it	18 milliseconds; 78 million years	Miller et al. (2000); Radzicka and Wolfenden (1995)	3
Largest kinetic isotope effect, hydrogen against deuterium, over the top at room temperature	about 7	Westheimer (1961)	3, 12
Gibbs free energy of forming: liquid water; ammonia gas; diamond	−237.14; −16.4; 2.900 kJ for each mole	Dean (1999), *Lange's Handbook of Chemistry*	3
Heats of forming the gases at 25 degrees Celsius: CO; CO_2; NO; NH_3	−110.53; −393.52; +90.29; −45.90 kJ for each mole	Chase (1998), as the NIST Chemistry WebBook gives them	3
Entropies of the gases at 25 degrees Celsius: CO; CO_2; NO; N_2; O_2; H_2; NH_3	197.66; 213.79; 210.76; 191.61; 205.15; 130.68; 192.77 J for each kelvin and mole	Chase (1998), as the NIST Chemistry WebBook gives them	3
Standard electrode potentials: Zn^{2+}/Zn; Cu^{2+}/Cu; Li^{+}/Li; oxygen against hydrogen	−0.7618; +0.3419; −3.0401; 1.229 V	CRC Handbook of Chemistry and Physics, 84th edition (2004)	1, 3
Heat of burning a mole of methane into carbon dioxide and liquid water	890 kJ (measured values −890.16 to −890.70 kJ)	NIST Chemistry WebBook, as collected by Cheméo	3
Haber process: temperature; pressure	400 to 500 degrees Celsius; above 100 bar	Appl (1997)	3
Share of the world's people fed by nitrogen fertilizer, 2008	48 percent	Erisman et al. (2008)	3
Nominal voltage of a lithium-ion cell	3.6 or 3.7 V	EL-CELL	1, 3, 14
Heat delivered by heat pumps in moderate climates	up to three times the energy they consume	U.S. Department of Energy, Solar Decathlon	2
Band seen by thermal cameras	about 8 to 14 micrometers	LightPath Technologies	2

Quantity	Value	Source	Chapters
Crystals			
Helium-4: least pressure for the solid at the lowest temperatures	about 25 bar	Souris et al. (2010)	5
Strongest X-ray line of copper, $K\alpha_1$	0.15405929(5) nm	Deutsch et al. (2004)	5
Density of rock salt (halite)	2.17 g per cubic centimeter	tables of the mineral halite	5
Speeds of sound: copper; iron; diamond; air at 20 degrees Celsius	4,664 (about 4,700); about 5,100; about 12,000; 343 m/s	CRC Handbook of Chemistry and Physics, as tabulated	5
Heat taken up by a mole at 25 degrees Celsius: copper; iron; lead; diamond	24.47; 25.09; 26.40; 6.115 J for each kelvin	CRC Handbook of Chemistry and Physics, as tabulated	5, 6
Debye temperatures: copper; lead; diamond; iron	343; 105; 2,230; about 470 K	Kittel (1996)	5, 6, 9, 12
Thermal conductivity: copper at 300 K; natural diamond at 25 degrees Celsius; diamond of 99.93 percent carbon-12; window glass	401; about 2,100; 3,150; 0.7 to 1.3 W for each meter and kelvin	Kittel (1996); Wei et al. (1993); Wei et al. (1993); Janssen and Warmoeskerken (2006)	5, 6
Diamond of 99.9 percent carbon-12: how fast it passes heat, against natural diamond	50 percent faster at room temperature	Anthony et al. (1990)	12
Stress for slip in metals, against the whole-plane estimate $G/2\pi$	a thousand to ten thousand times lower	Frenkel (1926); Taylor (1934); Orowan (1934); Polanyi (1934)	5
Carbon in plain carbon steel; chromium in stainless steel	0.02 to 2.14 percent by weight; at least 10.5 percent	the standard definitions of steel; for stainless steel, EN 10088-1 (European Committee for Standardization)	5
Track pitch of the compact disc	1.6 micrometers	IEC 60908 (International Electrotechnical Commission)	5
Structures held in the Protein Data Bank on 21 May 2026; share found by X-ray diffraction	254,149; about 80 percent	Protein Data Bank	5

Quantity	Value	Source	Chapters
Frequency of the quartz crystals of watches and clocks	32,768 Hz (2^{15})	the standard frequency of the crystals of watches and clocks	5
Electrons in solids			
Resistivities at 20 degrees Celsius: copper; silver; aluminum; pure silicon; window glass; fused quartz	1.678×10^{-8}; 1.59×10^{-8}; 2.65×10^{-8}; about 2.3×10^{3}; 10^{11} to 10^{15}; 7.5×10^{17} ohm meters	standard tables of resistivity	6
Rise of copper's resistance near room temperature	about 0.4 percent for each kelvin	standard tables of resistivity	6
Densities at 20 degrees Celsius: copper; aluminum; sodium	8.935; 2.70; 0.9688 g per cubic centimeter	standard tables of the elements	6, 11
Heat taken up by copper's electrons, γ in $C = \gamma T$	0.695 thousandths of a joule for each mole and each kelvin squared	Kittel (1996)	6
Ratio of heat to charge conduction, over the temperature, for copper at 0 degrees Celsius	2.23×10^{-8} watt ohms for each kelvin squared	Kittel (1996)	6
Band gaps at 300 K: germanium; silicon; gallium arsenide; cadmium sulfide; gallium nitride; diamond	0.66; 1.12; 1.42; 2.42; 3.4; 5.47 eV	Sze and Ng (2007)	6, 7, 14
Band gap of silica	about 9 eV	Tropf, Harris and Thomas (2000)	6
Electrons lifted across the gap in pure silicon at 300 K	1.0×10^{10} in each cubic centimeter	Sproul and Green (1991)	6, 7, 14
Silicon: atoms in each cubic centimeter; side of its cubic cell; dielectric constant	5×10^{22}; 0.543 nm; 11.7	standard tables of the properties of silicon	6, 7
Silicon: states of its conduction band within kT of the bottom, at 300 K	about 3×10^{19} in each cubic centimeter	standard tables of the properties of silicon	7
Effective masses of conduction electrons: gallium arsenide; silicon, along one axis and across it	0.067 m_e; 0.98 m_e and 0.19 m_e (0.26 m_e averaged, computed)	Sze and Ng (2007)	6, 7, 10
Binding of the phosphorus donor in silicon; of the boron acceptor	0.045 eV; 0.045 eV	Sze and Ng (2007); standard tables of the properties of silicon	7, 14

Quantity	Value	Source	Chapters
Extent of the phosphorus donor's orbit in silicon	about 2.5 nm	Zwanenburg et al. (2013)	7
Wavelength below which sodium films turn clear	210 nm	Wood (1933)	6
Onset of the d bands' absorption: copper; silver	near 2 eV; near 4 eV	Ehrenreich and Philipp (1962)	6
Excitons of cuprous oxide: highest level followed; its extent	n = 25; more than two micrometers	Kazimierczuk et al. (2014)	6
Indium tin oxide: gap; resistivity; share of visible light a thin film passes	about 4 eV; near 10^{-6} ohm meters; more than four-fifths	Kim et al. (1999)	6, 14
Most that one junction turns of sunlight into power	30 percent, at a gap of 1.1 eV	Shockley and Queisser (1961)	7
Light for each watt: best white LEDs; filament bulbs; fluorescent lamps	just over 300; 16; close to 70 lumens	Nobel Foundation (2014)	7
Share of the world's electricity used for lighting	about a fourth	Nobel Foundation (2014)	7
Transistors in one processor (Apple, 2020)	16 billion	Apple (2020)	7
Magnets			
Curie points: cobalt; nickel; gadolinium; magnetite; neodymium-iron-boron magnets	1400 K; 627 K; 293.2 K; 858 K; about 583 to 673 K	standard tables of magnetic materials; standard tables of permanent magnets	8
Néel temperatures: manganese oxide; nickel oxide; chromium	116 K; 525 K; 308 K	standard tables of magnetic materials	8
Iron: side of its cubic cell at 20 degrees Celsius; density	286.65 pm; 7.874 g per cubic centimeter	standard tables of the elements	8
Moments for each atom in the metals at the lowest temperature: iron; cobalt; nickel	2.22; 1.72; 0.606 Bohr magnetons	Kittel (1996)	8
Anisotropy constants K_1 at room temperature: iron; nickel; cobalt	4.8×10^4; -0.5×10^4; 45×10^4 J for each cubic meter	standard tables of magnetic materials	8

Quantity	Value	Source	Chapters
Susceptibilities at 20 degrees Celsius: copper; water	-9.63×10^{-6}; -9.035×10^{-6}	standard tables of magnetic susceptibilities	8
Remanence of a neodymium-iron-boron magnet	typically 1.3 T	standard tables of permanent magnets	8
Critical exponent β: order of any direction in three dimensions; order along one axis	0.3689(3); 0.32641871(75)	standard tables of critical exponents	8
Single-domain grains; domains of a large crystal	about 25 to 80 nm; about 10^{-6} to 10^{-4} m	standard accounts of magnetic domains	8
Superfluids and superconductors			
Helium-4: change to a superfluid at the pressure of its vapor; boiling point at the pressure of the air	2.1768 K; 4.2 K	standard tables of liquid helium	9, Brief
Liquid helium-4 at the lowest temperatures: density; speed of sound; rotons' least energy and its momentum	0.145 g per cubic centimeter; about 238 m/s; k times about 8.6 K, at ħ times about 1.9 per ångström	Donnelly and Barenghi (1998)	9
Superfluid helium-4: share of atoms in the lowest state of motion; speed at which flows in tubes break down; second sound near 1.8 K	about 8 percent; of order 20 cm/s; about 20 m/s	standard accounts of liquid helium; Peshkov (1944)	9
Helium-3: change to a superfluid at zero pressure; on its melting curve; the two changes first found	0.93 thousandths of a kelvin; 2.491 thousandths of a kelvin; near 2.7 and 1.8 thousandths of a kelvin	Greywall (1986); standard tables of the helium-3 superfluid; Osheroff, Richardson and Lee (1972)	9
Transition temperatures: aluminum; tin; mercury; lead; niobium	1.20; 3.72; 4.15 (4.2, as Kamerlingh Onnes found it); 7.19; 9.26 K	standard tables of superconductors; Kamerlingh Onnes (1911)	9, 14, Brief
Least energy to break a pair, 2Δ, as a multiple of kT_c: aluminum; lead	3.4; 4.3	Kittel (1996)	9, Brief
Coherence lengths: aluminum; lead; niobium	1,600; 83; 38 nm	Kittel (1996)	9
Penetration depths	typically 50 to 500 nm	standard tables of superconductors	9

Quantity	Value	Source	Chapters
Critical fields: aluminum; tin; lead; niobium-titanium; niobium-tin	0.01; 0.03; 0.08; about 15; about 30 T	standard tables of superconductors	9
Lifetime of a current in a superconducting ring	more than 100,000 years (a lower bound)	File and Mills (1963)	9
Transition temperatures of later superconductors: lanthanum barium copper oxide; yttrium barium copper oxide; copper oxides with mercury; magnesium diboride; the first of iron and arsenic; hydrogen sulfide at 155 billion pascals	near 35 K; 92 K; above 130 K; 39 K; 26 K; 203 K	Bednorz and Müller (1986); standard tables of superconductors; Nagamatsu et al. (2001); Kamihara et al. (2008); Drozdov et al. (2015)	9
Liquid nitrogen's boiling point	77 K	standard tables of superconductors	9
Scanners for magnetic resonance imaging: fields; number in use	mostly 1.5 T, also 3 T; around 50,000	standard accounts of medical imaging; standard accounts of MRI	9, 12
Large Hadron Collider: ring; dipole magnets; their field; their temperature; superfluid helium	27 km; 1,232; up to 7.7 T; 1.9 K; 96 tonnes	standard accounts of the Large Hadron Collider	9
Superconducting tape of yttrium barium copper oxide at 77 K	more than 500 A for each centimeter of width	standard accounts of superconducting wire	9
Helium in natural gas	up to seven percent	standard accounts of liquid helium	9
Numbers kept exactly			
Josephson ratio in different superconductors	the same to within 2 parts in 10^{16}	Tsai, Jain and Lukens (1983)	10
Josephson voltage standards	some twenty thousand junctions; microwaves near 75 GHz; up to ten volts	standard accounts of the Josephson voltage standard	10
Hall resistance in gallium arsenide and in graphene	the same to within about one part in 10^{10}	Janssen et al. (2012)	10, Brief
Von Klitzing's discovery	a silicon transistor at 1.5 K, in fields up to 18 T, February 1980	von Klitzing, Dorda and Pepper (1980)	10
	e/3; e/4		10

Quantity	Value	Source	Chapters
Charges carried in the fractional states at 1/3 and at 5/2		de-Picciotto et al. (1997); Saminadayar et al. (1997); Dolev et al. (2008)	
Magnetic fields of the brain at the scalp; the Earth's field; magnetic noise of a city	about 10 fT; some fifty millionths of a tesla; about 10^{-7} T	standard accounts of magnetoencephalography	10
Helmets for magnetoencephalography	about three hundred SQUIDs	standard accounts of magnetoencephalography	10
Light in matter			
Refractive indices at 589 nm: air at 0 degrees Celsius and 1 atmosphere; water; fused silica; crown glass; diamond	1.000293; 1.333; 1.458; 1.50 to 1.54; 2.417	standard tables of refractive indices	11
Indices of calcite at 590 nm	1.658 and 1.486	standard tables of birefringence	11
Index of magnesium fluoride	1.38	standard optics	11
Rainbow: angles from the point opposite the sun, red and violet	about 42 and about 40 degrees	standard accounts of the rainbow	11
Optical fiber: indices of core and cladding near 1,500 nm; loss near 1,550 nm; loss of the first low-loss fiber, 1970	about 1.4475 and 1.444; about 0.2 decibels in each kilometer; 17 decibels in each kilometer	standard accounts of optical fibers	11
Laser wavelengths: ruby; doubled neodymium laser and its source; argon fluoride; carbon dioxide	694.3 nm; 532 and 1,064 nm; 193 nm; 10.6 micrometers	Franken et al. (1961); Maiman (1960); standard accounts of lasers	11
Scattering of light by light	evidence 2017; observation 2019	ATLAS Collaboration (2017; 2019)	11
Visible light: wavelengths; energies of its photons	about 380 to 750 nm; about 1.65 to 3.26 eV	standard accounts of vision	6, 11, 14
Arms of the LIGO interferometers	4 km	Abbott et al. (2016)	11
The nucleus seen in matter			

Quantity	Value	Source	Chapters
Heavy water: mass of a liter; freezing point; boiling point	about 1.107 kg; 3.82 degrees Celsius; 101.4 degrees Celsius	standard tables of the properties of heavy water	12
Vibrational constants of H_2 and D_2; their ratio; zero-point energy of H_2	4401.213 and 3115.50 per centimeter; 0.708; about 0.27 eV (computed)	Huber and Herzberg (1979), as the NIST Chemistry WebBook gives them	12
Deuteron electric quadrupole moment	$0.285699(15)(18)$ e fm^2	Puchalski, Komasa and Pachucki (2020), as *The Alphabet of Particles* gives it	12
Sodium's yellow light (the D_2 line): energy of its photon; mean life of its upper state	2.104 eV; 16.25 ns	Volz et al. (1996)	12
Holmium-163 heavier than dysprosium-163, as atoms	2.833 keV ($2833 \pm 30 \pm 15$ eV)	Eliseev et al. (2015)	12
Shielding constant of the hydrogen molecule; its deshielding part	2.68×10^{-5}; -0.56×10^{-5}	Ramsey (1950)	12
Masses of the molecules of uranium hexafluoride carrying uranium-235 and uranium-238	349.03 and 352.04 u	standard accounts of isotope separation	12
Proton resonance in the strongest magnets made for chemistry	about 28 T, 1.2 GHz	standard accounts of NMR and MRI	12
Range of the chemical shifts in organic molecules: protons; carbon-13	about ten parts in a million; about two hundred	standard accounts of NMR	12
Shift of iron-57's gamma ray over 22.5 m of height	$(2.56 \pm 0.25) \times 10^{-15}$; later read to about one percent of its size	Pound and Rebka (1960); Pound and Snider (1964)	12
Strontium clock: frequency of its clock transition	429,228,004,229,873 Hz	the frequency the International Bureau of Weights and Measures recommends; standard accounts of atomic clocks	12
Strontium clock: shifts from its surroundings measured and taken out	to 8.1 parts in 10^{19}	Aeppli et al. (2024)	12

Quantity	Value	Source	Chapters
Hydrogen's hyperfine splitting, the 21 cm line	1420.405751768(2) MHz	Hellwig et al. (1970)	12
Best cesium clocks	about one part in 10^{16}	standard accounts of atomic clocks	12
International Atomic Time	about 450 clocks in some 80 laboratories	standard accounts of atomic clocks	12
Clocks of the Global Positioning System: how much faster than the ground they run; their set frequency	about 38 microseconds a day; 10.22999999543 MHz	Ashby (2003); standard accounts of the Global Positioning System	12, 14
Oxygen-18 in the shells of foraminifera	0.22 parts in a thousand more for each degree of cooling	Epstein et al. (1953)	12
Stars			
Mass of Sirius B; period of its orbit with Sirius A	1.018 ± 0.011 solar masses; 50.13 years	Bond et al. (2017)	13
Radius of Sirius B	about 5,600 km (computed from its gravitational redshift, 80.65 ± 0.77 km/s)	Joyce et al. (2018)	13
Mass of the Sun; radius of the Earth	1.988×10^{30} kg; 6,371 km	International Astronomical Union (2015); standard tables	13
White dwarfs: temperature inside; mass of the commonest	some ten million kelvin; about 0.6 solar masses	standard accounts of white dwarfs	13
PSR J0740+6620: mass; radius	2.08 ± 0.07 solar masses; 13.7 km $(+2.6, -1.5)$	Fonseca et al. (2021); Miller et al. (2021)	13
Masses of most neutron stars weighed	near 1.4 solar masses	standard accounts of neutron stars	13
GW170817: date; masses together; masses of the two stars; distance	17 August 2017; about 2.74 solar masses; 1.17 to 1.60 solar masses; about 40 megaparsecs	Abbott et al. (2017), *Physical Review Letters*	13
GW170817: delay of the gamma rays; bound on the difference between the speeds of gravitational waves and light	about 1.74 s; between -3×10^{-15} and $+7 \times 10^{-16}$ of c	Abbott et al. (2017), *Astrophysical Journal Letters*; *The Gravitational Passage*, Chapter 16, Section V	13
Pulsars: the first found; the Crab pulsar; the fastest known	a pulse every 1.34 s; a turn every 33 ms; 716 turns each second	Hewish et al. (1968); standard accounts of pulsars	13

Quantity	Value	Source	Chapters
The pulsar of Hulse and Taylor, PSR B1913+16: period of its orbit	7.75 hours	Hulse and Taylor (1975)	13
Pulsars timed for a background of gravitational waves	67, over 15 years	NANOGrav Collaboration (2023)	13
History in use			
The Hindenburg disaster	6 May 1937, at Lakehurst, New Jersey; 36 people died	standard accounts of the Hindenburg disaster	1

Notes

The Ladder in Brief

1. Proton and neutron. The proton's charge radius, 0.84075 $\pm$ 0.00064 fm, and its mass, 938.27208943 $\pm$ 0.00000029 MeV, are the values recommended in 2022 by the Committee on Data of the International Science Council (CODATA; Mohr et al., 2025), as Volume One, Chapter 8, Section VIII, and Chapter 2, Table 2.1, give them; Chapter 1, Table 1.1, of this volume gives the same mass, and Chapter 1, Section IX, gives the radius as 0.84 fm. That about 99 percent of the proton's mass is the energy of its binding is the finding of *The Strengths of the Kinds*, Chapter 6, Section I: of the proton's 938 MeV the three quarks supply about 9 MeV, and the color field and the motion of the quarks and gluons supply the rest (Chapter 1, Section III; Volume One, Chapter 2, Section VII). Lattice computation of the theory of color, solved by computer on a grid of points in space and time, gives the nucleon's mass as 936 $\pm$ 25 $\pm$ 22 MeV against the measured 939 MeV (Dürr et al., 2008; Volume One, Chapter 2, Section VII).

2. Nucleus. The reach of the force between nucleons, 1.41 fm, is the pion's own length, $\hbar c/(m_\pi c^2)$ = 197.327 MeV fm divided by 139.570 MeV, with the charged pion's mass from the Particle Data Group, 2026 (Chapter 1, Box 1.1; Volume One, Chapter 1, Box 1.1, and Chapter 4, Box 4.1). The radius of a nucleus, about 1.2 $A^{1/3}$ fm, is that of Krane (1987), as Volume One, Chapter 4, Section VI, gives it and Chapter 1, Section IX, restates it; for helium-4 it is 1.2 $\times$ $4^{1/3}$ = 1.9 fm, and for uranium-238 it is 1.2 $\times$ $238^{1/3}$ = 7.4 fm (computed). The deuteron is bound by 2.2246 MeV (Volume One, Chapter 4, Section VIII, from the masses of CODATA 2022), which is 1.11 MeV for each of its two nucleons (computed). Iron-56 is bound by 492.26 MeV, which is 8.790 MeV for each nucleon, and nickel-62 by 545.26 MeV, which is 8.795 MeV for each nucleon; both are computed from the

atomic masses of the National Institute of Standards and Technology's table, as Volume One, Chapter 4, Box 4.2, computes them, and both round to 8.79 MeV, the top of the binding curve (Volume One, Chapter 4, Figure 4.1), which Chapter 1, Section IX, gives as about 8.8 MeV.

3. Atom. Hydrogen's ground state has the size of the Bohr radius, $\hbar/(m_e c\alpha) = 52.9$ pm, with the constants of CODATA 2022 (Chapter 1, Box 1.4, which gives it as 0.529×10^{-10} m; Volume One, Chapter 7, Box 7.1). The ion of cesium, Cs^+, with eight neighbors of opposite charge, has a radius of 174 pm (Shannon, 1976, as Volume One, Chapter 11, Section X, gives it). Hydrogen is bound by 13.598 eV, the binding with the proton's small recoil counted (Chapter 1, Section VI; Volume One, Chapter 7, Section IX). The energies needed to free the most loosely held electron of cesium and of helium are 3.89390572743 eV and 24.587389011 eV (Kramida et al., 2024, as Volume One, Chapter 11, Section X, and Chapter 9, Table 9.2, give them); Chapter 1, Section VII, gives helium's as 24.6 eV. The innermost electron of barium, in its K shell, the shell of $n = 1$, is bound by 37,441 eV (Thompson et al., 2009, Table 1-1, as Volume One, Chapter 9, In Use, gives it).

4. Molecule. The bond lengths are those of the National Institute of Standards and Technology's Computational Chemistry Comparison and Benchmark Database: 74.1 pm for the hydrogen molecule, H_2, and 267.3 pm for the lithium molecule, Li_2 (Johnson, 2022, as Volume One, Chapter 11, Table 11.1, gives them). The energies needed to separate the molecules into their atoms are 1.0 eV for Li_2 (Huber and Herzberg, 1979); 9.80 eV for the nitrogen molecule, N_2, computed from 945.41 kJ for each mole (Greenwood and Earnshaw, 1997); and 4.478 eV for H_2, from 36,118.06962 waves for each centimeter (Liu et al., 2009); Volume One, Chapter 11, Table 11.1 and Section XVI, gives all three, and Chapter 1, Table 1.2, restates those of H_2 and N_2 as 4.48 and 9.8 eV. Two water molecules held by one hydrogen bond need 0.137 eV to be pulled apart (Rocher-Casterline et al., 2011, as Volume One, Chapter 11, Section XIV, gives it). Two helium atoms, held by the dispersion force alone, are bound by the Boltzmann

constant times 1.1 thousandths of a kelvin (Grisenti et al., 2000, as Volume One, Chapter 11, Section V, gives it), which is 9.5×10^{-8} eV (computed); Chapter 1, Table 1.2, gives it as about 0.0000001 eV. Chapter 3 of this volume takes up how molecules change into one another.

5. Liquid and solid. The energies needed to take a metal apart into free atoms are 1.113 eV for each atom of sodium and 8.90 eV for each atom of tungsten, and the energy needed to take a crystal of salt apart into free ions is 7.94 eV for each pair of ions (Kittel, 2005, as Volume One, Chapter 11, Table 11.2, and Chapter 11, Section X, give them); Chapter 1, Table 1.2, restates them as 1.1, 8.9 and 7.94 eV. Chapters 4 to 7 of this volume take up liquids, crystals, the bands of electron states in solids, and semiconductors.

6. Ordered states. Iron loses its alignment as a magnet at its Curie point, 1043 kelvin (standard tables of magnetic materials, as Chapter 8, Section V, gives it); with the Boltzmann constant, $8.617333262 \times 10^{-5}$ eV for each kelvin (CODATA 2022), the energy kT at that temperature is 0.0899 eV, which rounds to 0.090 eV (computed; Chapter 14, Table 14.1, gives the same). Lead becomes a superconductor below 7.19 kelvin (standard tables of superconductors, as Chapter 9, Section VI, gives it), and the least energy that breaks one of its pairs of electrons is 4.3 times kT at that temperature (Kittel, 1996, as Chapter 9, Section VIII, gives it), which is 0.0027 eV (computed). Chapter 10 takes up the whole numbers that such states keep exactly.

Chapter 1. From Wholes to Gatherings

1. Section II, the Incommensuration Theorem. *The Quantum Passage*, Chapter 4, Section II, states the Incommensuration Theorem in the words the section quotes. The same chapter of that book, Section IV, gives the three axioms of *An Immanent Metaphysics*, Axiom I, Axiom II and Axiom III, in the exact wording of that book, aphorism 1.3-1, and its Section V derives the three axioms from the theorem. *Incommensuration; The Theorem and the Three Axioms* sets out the theorem and the axioms in full.

2. Section IV and Box 1.2, exclusion from the principle of identity. *The Quantum Passage*, Chapter 8, Section VI, from which Box 1.2 takes its steps, derives the two ways in which particles of one kind share states from the principle of identity applied to two poles of the act of comparison. Of the instances of the first pole *An Immanent Metaphysics*, aphorism 1.46-12, says that they are "local and interexclusionary", and of the instances of the second that they are "non-local and intercompositional"; *Incommensuration; The Theorem and the Three Axioms*, premise P7, states the same. Applied to the first pole, the principle of identity gives exclusion, the rule of the particles of matter; applied to the second, it gives addition in one state, the rule of the carriers of the forces. In this volume the rule of Box 1.2 is a premise of the two kinds of filling of Chapter 2, Box 2.5, of the two electrons for each cell in a band of Chapter 6, Box 6.2, of the gathering of even wholes and of helium-4 and helium-3 in Chapter 9, Sections II and V, of the multiplying of light in Chapter 11, Section XIII, and of the pressure of a filled Fermi sea in Chapter 13, Section II.

Chapter 2. The Counting of Ways

1. Section VI, the two directions of time. *Measurement*, Chapter 12, Section VII, which the section quotes, names the first of the two directions, the direction of time read from the order of acts, as "the direction of the cycle of Axiom II", Axiom II being the second of the three axioms of *An Immanent Metaphysics* (Chapter 1, Note 1). The same section of *Measurement* shows that the two directions point the same way wherever both are found, since "each act of recording joins the two arrows in one event". Section VI of this chapter applies that joining to the count of microstates: the traces that the particles make of one another stay once they have reached many particles, and their staying, counted over the microstates, is the growth of entropy.

Chapter 10. Steps Kept Exactly

1. Section X, the Planck constant as a value. *The Strengths of the Kinds*, Chapter 1, Section II, which Section X cites for the ratio of the von Klitzing constant to the impedance of empty space, states the tie of ħ to *An Immanent Metaphysics*, in the frame of the six aspects present in every comparison, which that book calls the intrinsics: "ħ joins actuality, the relation of force to time, to potentiality, the relation of probability to possibility; in the frame of the intrinsics ħ is the relation of potentiality to actuality".

Terms

Absorption

Matter taking up light near its natural frequencies, passing the wave's energy on to the atom's other motions or lifting the atom to a higher level. (Chapter 11)

Acceptor

An added atom with one fewer outer electron than the crystal's atoms, which gives a hole to the valence band. (Chapter 7)

Acoustic and optical modes

The modes of a crystal whose longest waves are sound; and, where a unit cell holds more than one atom, the modes in which its atoms move against one another. (Chapter 5)

Action (*of a field*)

The quantity, added up over space and time, that every small change of the field's potential leaves unchanged when the field's laws hold. (Chapter 9)

Activation energy

The energy E_a by which the transition state of a reaction lies above its start. (Chapter 3)

Actinides

The second run of the f block, actinium to lawrencium. (Chapter 1)

Aharonov-Bohm phase

The turning of a charge's phase, carried round a loop, by its charge times the magnetic flux through the loop, divided by ħ, even where the charge meets no field. (Chapter 10)

Alkali metals

Group 1 of the periodic table, whose atoms have one electron beyond a closed shell. (Chapter 1)

Alkaline earth metals

Group 2 of the periodic table. (Chapter 1)

Alloy

A metal made of more than one element. (Chapter 5)

Alpha particle

The helium-4 nucleus, two protons and two neutrons filling the lowest state, bound by 28.30 MeV. (Chapter 1)

Amorphous solid

A solid with no repeat in its arrangement, amorphous meaning without form; a glass is the commonest kind. (Chapter 4)

Amphiphile

A molecule with one end drawn to water and the other shunning it, such as soap. (Chapter 4)

Amplitude

The height of a particle's wave at each place; the chance of finding the particle there grows as its square. (Chapters 9 and 10)

Angle-resolved photoemission

Light knocks electrons out of a surface, and the energies and directions with which they leave give the energy and momentum they had inside. (Chapter 10)

Angular momentum

The measure of turning motion, for a body going round a center its momentum times its distance from the center, kept because the laws of nature are the same in every direction. (Preface; Chapter 1)

Anode; cathode

The electrode of a cell at which oxidation takes place; and the electrode at which reduction takes place. (Chapter 3)

Antibonding state

The higher of the two levels into which one level of each of two atoms becomes, in which the two parts of the electron's state cancel between the nuclei; it is raised more than the bonding state is lowered. (Chapter 1)

Antiferromagnet

A crystal whose neighboring spins alternate, with moments that cancel. (Chapter 8)

Antiparticle

A particle of the same mass as another, with its electric charge and every other such label reversed. (Preface; Chapter 1)

Arrhenius law

The rate of a reaction over its barrier, $A\, e^{-E_a/kT}$: the share of the ways that place E_a in the moving part, times a prefactor of attempts and of counts of states (Box 3.1). (Chapter 3)

Atom

A nucleus with electrons bound to it by the electric pull between the nucleus's positive charge and their negative ones; "atomic" means of the atom. (Preface; Chapter 1)

Atomic clock

A count of the cycles of light matching a transition of an atom; a standard because atoms of one kind cannot be told apart, so the frequency is the same for every such atom everywhere in the universe. (Chapter 12)

Atomic mass unit (u)

A twelfth of the mass of an atom of carbon-12, 931.49410372 MeV/c^2. (Chapter 2)

Atomic number (Z)

The number Z of a nucleus's protons, which is the charge of the atom's nucleus, counts the atoms and places each element in the periodic table. (Chapter 1)

Avogadro constant; mole

A mole is $6.02214076 \times 10^{23}$ molecules, the Avogadro constant, exact by the definition of the mole. (Chapter 2)

Band

The set of electron states in a crystal that grow from one state of the single atom, as many as the crystal has cells, wider the more the atoms' waves overlap. (The Ladder in Brief; Chapter 6)

Band gap (gap)

A range of energy with no electron state in the crystal; it lies between two bands wherever no band reaches across, and overlapping bands leave none. (The Ladder in Brief; Chapter 6)

Bar

A pressure of 100,000 pascals, about the pressure of the air. (Chapter 3)

Bargmann's bound

A pull of short reach binds two particles only when its strength passes a threshold, because confinement costs energy. (Chapter 9)

Barrier

A range of distance in which a particle would need more energy than it has; for a reaction, the arrangement of highest energy that a rearrangement passes through (Chapter 3); for a p-n junction, the rise in electron energy across its depletion layer, whose height is $(kT/e)\ \ln(N_{acc}N_{don}/n_i^2)$ as a voltage, with N_{acc} and N_{don} the numbers of acceptors and donors in each unit of volume (Chapter 7). (Chapters 1, 3 and 7)

Baryon

A whole of three quarks, one of each color. (Chapter 1)

Baryon number

The number of baryons less the number of their antiparticles; every change at the temperatures of the present universe keeps it. (Chapter 1)

BCS theory

The account of superconductivity of Bardeen, Cooper and Schrieffer. (Chapter 9)

Beer-Lambert law

The fall of the strength of light that matter absorbs as the exponential of the thickness it crosses. (Chapter 11)

Berry phase

The extra turn of phase a state gathers when carried slowly round a closed loop of its settings. (Chapter 10)

Beta decay

The turning of a neutron of a nucleus into a proton, or a proton into a neutron, by the weak force, with an electron or a positron and a neutrino given off; a proton can also become a neutron by taking in an atomic electron. (Chapter 1)

Binding energy

The energy that must be supplied to separate a bound whole into its parts; for hydrogen, 13.598 eV. (Preface; Chapter 1)

Birefringence

Double refraction: a crystal not alike in every direction slows the two linear polarizations differently and splits a beam in two. (Chapter 11)

Bit

The smallest piece of information, one choice between two. (Chapters 2 and 8)

Black body; black-body radiation

A body that takes in all the light that falls on it; and the light in balance with matter at one temperature, which such a body sends out. (Chapter 2)

Black hole

A body whose gravity lets nothing out. (Chapter 13)

Bloch's theorem; Bloch state

The states of an electron of definite energy in a crystal can be chosen so that each, shifted by one step of the lattice, is the same state turned forward by a phase that is the same at every step (Box 6.1); such a state belongs to the whole crystal. (Chapter 6)

Bohr magneton

$e\hbar/(2m_e)$, the moment of one unit $\hbar$ of orbital angular momentum, $9.2740100657 \times 10^{-24}$ joules for each tesla; the electron's spin carries one; it is the natural unit of the electron's magnetic moment. (Chapters 1 and 8)

Bohr radius (a_0)

The size of hydrogen's ground state, $a_0 = \hbar/(m_e c\alpha) = 0.529 \times 10^{-10}$ m, where the cost of confinement balances the pull (Box 1.4): the electron's own length divided by α. (Chapter 1)

Boltzmann constant (k)

$k = 1.380649 \times 10^{-23}$ J/K, exact since 2019, a unit that converts a temperature in kelvin to an energy; the kelvin is the unit of temperature. (The Ladder in Brief; Chapter 2)

Boltzmann factor

$e^{-E/kT}$, the weight with which a small part of a large system at temperature T takes a state of energy E; the share of the ways that place an extra energy E in one part of a gathering at temperature T. (Chapters 2 and 14)

Bond

Two atoms held together by electrons in a lower shared state. (Preface; Chapter 1)

Bond length

The separation of least energy, where the shared electrons' pull and the nuclei's push balance. (Chapter 1)

Bonding state

The lower state of an electron shared by two atoms: the lower of the two levels into which one level of each of two atoms becomes, in which the two parts of the electron's state add between the nuclei. (Chapter 1)

Bose-Einstein condensation

The gathering of a large share of a cold gas of bosons into its one lowest state; more widely, of a large share of bosons, or of wholes made of an even number of fermions, into the one lowest state, below the temperature at which their thermal wavelength reaches about their spacing (Box 9.1). (Chapters 2 and 9)

Boson

A particle whose spin is a whole number, such as the photon, of which any number can share a state. (Preface; Chapters 1, 2 and 14)

Bound-state beta decay

A beta decay that places its new electron in an empty bound state of a stripped atom, so that an atom stable when whole decays when stripped. (Chapter 12)

Bragg's law

$n\lambda = 2d \sin \theta$: X-rays of wavelength λ leave planes of spacing d in a strong beam only at those glancing angles θ. (Chapter 5)

Bravais lattices

The 14 kinds of lattice in three dimensions. (Chapter 5)

Brewster's angle

The angle, $\tan \theta_B = n_2/n_1$, at which only the polarization across the plane of incidence is reflected, because the driven electrons send nothing along their line of swing. (Chapter 11)

Brillouin zone

The single cell of the reciprocal lattice, centered on zero, in which every state's wave vector can be placed. (Chapter 6)

Brownian motion

The ceaseless wandering of a small particle in a liquid or gas, struck unevenly by the molecules round it. (Chapter 4)

Carnot's limit

No engine working between T_h and T_c turns more than $1 - T_c/T_h$ of the heat it takes in into work. (Chapter 2)

Carrier of a force

The particle through which a force acts between two others. (Chapter 1)

Carrier of charge

An electron or a hole that carries a current (a second sense of "carrier", apart from the carriers of the forces of Chapter 1). (Chapter 6)

Catalyst

A substance that opens a route of lower barrier and is left unchanged, speeding a reaction both ways alike and leaving where the reaction settles unchanged; an enzyme is a catalyst made by a living cell. (Chapter 3)

Cauchy and Sellmeier formulas

The forms in which a refractive index is written: a constant with a term in one over the wavelength squared; and a sum of one term for each natural frequency. (Chapter 11)

Chandrasekhar mass

The greatest mass that electrons' degeneracy pressure can hold up, about 1.4 times the Sun's mass for matter of two nucleons to each electron, set by ħ, c, G and the nucleon's mass (Box 13.2). (Chapter 13)

Chemical equilibrium

The settled state of a reaction, in which it runs as fast forward as backward. (Chapter 3)

Chemical potential (μ)

μ, the energy that adding one particle brings at fixed entropy and volume; particles pass from higher μ to lower; zero for photons. (Chapters 2 and 13)

Chemical shift

The move of a nucleus's resonance, in parts per million, set by the states of the electrons round it, and so by its bonds. (Chapter 12)

Chern insulator

A crystal whose bands wind with time reversal broken by magnets within it, a quantum anomalous Hall insulator. (Chapter 10)

Chern number

The winding of the filled states of a sheet or a crystal, equal to its Hall conductance in units of e^2/h. (Chapter 10)

Cherenkov radiation

The cone of light trailing a charged particle that moves through matter faster than c/n. (Chapter 11)

Chiral

Not the same as its mirror image, as a left hand is not the same as a right. (Chapter 11)

Circular dichroism

The unequal taking up by a chiral material of the two circular polarizations of light. (Chapter 11)

Classical limit

States so sparsely taken that both distributions, the Fermi-Dirac and the Bose-Einstein, reduce to the Boltzmann factor. (Chapters 2 and 13)

Clausius-Clapeyron relation

$dP/dT = L/(T\Delta v)$, the slope of a line of the phase diagram (Box 4.3). (Chapter 4)

Clausius-Mossotti relation

$(n^2 - 1)/(n^2 + 2) = N\alpha_p/(3\varepsilon_0)$, the index of a dense material from the polarizability of its molecules. (Chapter 11)

Cleavage

The parting of a crystal along a flat plane of its lattice; ionic crystals cleave where both new faces carry balanced charge. (Chapter 5)

Closed subshell

A subshell with every one of its states taken. (Chapter 1)

CODATA

The Committee on Data of the International Science Council, whose recommended values of the constants this book uses. (Chapter 1)

Coherence

The keeping of one phase over a beam of light. (Chapter 11)

Coherence length

The size of a Cooper pair. (Chapter 9)

Collective excitation

A motion shared by many particles at once that comes in quanta, such as a phonon, a hole or a magnon; it exists only while its gathering does and is not a kind of particle. Any number of phonons can share a mode, and they stand apart from the kinds of particle; the regions that carry the fractional charges $e/3$ and $e/4$ in the fractional states are collective excitations of the gathering of electrons, not kinds of particle. (The Ladder in Brief; Chapters 5, 10 and 14)

Colloid

Small particles or droplets, between about a billionth and a millionth of a meter across, held scattered through another substance. (Chapter 4)

Color

The charge of the strong force, a name with nothing to do with visible color. (Preface; Chapter 1)

Color center

An electron trapped at a vacancy of a crystal, which takes up light of one color. (Chapter 6)

Composite fermions

Electrons each bound to two flux quanta, filling whole levels of their own at the fractions $p/(2p + 1)$; they are collective excitations of the gathering of electrons. (Chapter 10)

Condensate

A gathering of many wholes into one state, with one amplitude and one phase across the whole of it; the share of its wholes in the lowest state of one whole's motion is one measure of it, nearly all of them in a thin gas and about eight percent in liquid helium-4. (Chapters 9 and 14)

Conduction band

The empty band above a semiconductor's last full band. (Chapter 6)

Confinement

The keeping of the color field within wholes that carry no color, so that no colored particle is found alone; and, in a second sense of the word, the confining of any particle to a small region, which costs it an energy of motion of about $\hbar^2/(2mr^2)$ for a particle of mass m within a distance r (Box 1.4), the cost of confinement. (The Ladder in Brief; Chapters 1 and 14)

Conjugate pair

Two quantities of which narrowing one widens the other: place and momentum, energy and time, angle and angular momentum. (Chapter 1)

Continuous change

A change in which the order grows from nothing at a point fixed by a symmetry that separates the ordered arrangement from the disordered one, with no latent heat. (Chapters 4 and 8)

Cooper pair

Two electrons just above a filled Fermi sea bound by any attraction however small, because they have nothing lower to fall to; an even whole (Box 9.2). (Chapter 9)

Cosmic microwave background

The light that went free when the first atoms formed, a black body today at 2.72548 kelvin. (Chapter 2)

Coulomb's law

The electric force between two charges falls as the inverse square of their distance; with the pull between unit charges $F = \alpha\hbar c/r^2$, the pull between the electron and the proton. (Chapter 1)

Count of states

The number of distinct ways one particle of a kind can be, apart from where it is and how it moves; a property of one particle, as distinct from the entropy of the whole. (Chapter 2)

Coupling

The strength with which a particle takes part in an interaction. (Preface)

Covalent bond

A bond made by a pair of electrons shared between two atoms; each bond is completed by a pair of electrons of opposite spin in the lower shared state. (Chapter 1)

Covalent, metallic, ionic and molecular solids

Solids held by shared pairs of electrons in fixed directions; by outer electrons shared among all the atoms, a bond with no direction; by the pull between ions of opposite charge; and by the weak pulls between whole molecules. (Chapter 5)

Critical angle

The angle, with sine n_2/n_1, beyond which no wave on the far side of a surface can match the phase. (Chapter 11)

Critical current

The current at which the push on a type II superconductor's threads tears them from the flaws that hold them, and resistance begins; for a Josephson junction, the largest current it can pass with no voltage. (Chapters 9 and 10)

Critical exponents

The powers that describe a change of order close to its point. (Chapter 8)

Critical field

The field that destroys the shared state of a type I superconductor; for a type II superconductor, the lower and the upper fields between which it lets a field in as threads. (Chapter 9)

Critical opalescence

The milkiness of a fluid near its critical point, from large fluctuations of its density. (Chapter 4)

Critical point

The temperature and pressure above which liquid and gas pass into each other with no jump; for water 647.096 kelvin and 22.064 million pascals (Box 4.2). (Chapters 2 and 4)

Crossing

The rule that allows a particle given off in a change to be replaced by its antiparticle taken in; by it, electron capture is the change of positron emission with the atom's electron taken in instead of a positron given off. (Chapter 12)

Crossover

A smooth change between arrangements with no jump and no point, where nothing separates them; a smooth change with no jump, found where nothing separates two arrangements. (The Ladder in Brief; Chapters 2, 8 and 14)

Crystal

A solid whose atoms stand in one arrangement repeated through space. (Preface; Chapter 5)

Crystal momentum

$\hbar\mathbf{k}$ for a Bloch state of wave vector $\mathbf{k}$, kept in every change up to a point of the reciprocal lattice. (Chapter 6)

Crystallographic restriction

A repeat can be turned onto itself by a half, a third, a quarter or a sixth of a turn and by no other part of a turn (Box 5.2). (Chapter 5)

Cuprates

Ceramic superconductors built of layers of copper and oxygen, with transition temperatures from 35 kelvin to above 130 kelvin. (Chapter 9)

Curie point

The temperature at which a magnet loses its alignment, at a point because a symmetry separates the arrangements; 1043 kelvin for iron. (The Ladder in Brief; Chapters 2 and 8)

Curie's law

A paramagnet's magnetization in a field grows as the field and falls as one over the temperature, $M = C\,B/T$ (Box 8.1). (Chapter 8)

Curie-Weiss law

Above the Curie point, a magnetization $C\,B/(T - T_C)$ (Box 8.2). (Chapter 8)

Curl

How much a quantity turns round a small loop at a place, for each unit of the loop's area. (Chapter 9)

Current

Charge passing a point each second, in amperes: charge in motion. (Chapters 3 and 6)

Curvature (of a band)

How sharply a band curves: the rate at which its slope changes with the wave vector. (Chapter 6)

Cyclotron motion

The turning of the electrons of a sheet at eB/m in a magnetic field. (Chapter 10)

Debye length

The distance $\sqrt{(\varepsilon_0 kT/(ne^2))}$ beyond which a plasma cancels the field of a charge. (Chapter 4)

Debye temperature (Θ)

The temperature Θ at which $k\Theta$ equals the quantum of a crystal's highest mode; it measures where the crystal's modes begin to freeze out. (Chapters 5, 9 and 12)

Debye T^3 law

The fall of a cold crystal's heat capacity as $(T/\Theta)^3$ (Box 5.3). (Chapter 5)

Decibel

A measure of loss, a loss of 10 decibels being a fall of the light to a tenth. (Chapter 11)

Decoherence

The passing of the relations of phase among a particle's alternatives into its joint state with what it interacts with. (Chapter 2)

Degeneracy pressure

The pressure a crowd of fermions exerts because exclusion holds most of them in states above the lowest; it needs no heat, and goes as $n^{5/3}/m$ for particles moving slowly and as $n^{4/3}$ for particles near c (Box 13.1). (Chapter 13)

Density of states

The number of states in each small range of energy near a given energy. (Chapter 6)

Depletion layer

The layer about a p-n junction emptied of carriers, with only the fixed charges of the dopants left in it. (Chapter 7)

Deshielding

In molecules, a second part of the electrons' change of the field a nucleus meets, of the opposite sign to the shielding, from the mixing of higher states. (Chapter 12)

Deuterium

Hydrogen whose nucleus holds a neutron beside its proton. (Chapters 3 and 12)

Deuteron

The nucleus of a proton and a neutron, of spin one, the only bound pair of nucleons: a proton and a neutron with spins aligned, bound by 2.2246 MeV. (The Ladder in Brief; Chapter 1)

Dielectric constant

The factor by which a solid weakens the electric pull between two charges placed in it; 11.7 for silicon. (Chapter 7)

Diffraction

The scattering of a wave by a regular arrangement into strong beams in a few directions. (Chapter 5)

Diffusion

The wandering of particles, by their random motion, from where they are many to where they are few. (Chapter 7)

Diamagnetism

The weak answer of every material to a field, against the field, from the change the field makes in the motion of all its electrons. (Chapter 8)

Diode; rectifying

A device that passes current one way and holds it back the other way; passing current one way only. (Chapter 7)

Diode law

$I = I_0(e^{eV/kT} - 1)$: the current through a junction grows as the Boltzmann factor of the forward voltage and settles at a small fixed value backward (Box 7.2). (Chapter 7)

Dipole pattern

A swinging charge sends out light most strongly at right angles to its swing and nothing along it. (Chapter 11)

Direct and indirect gaps

A gap whose band edges lie at one wave vector, so a photon alone can lift an electron across; and one whose edges lie at different wave vectors, so a phonon must take part. (Chapter 6)

Dirac particle

A particle distinct from its antiparticle; the neutrino is one. (Preface)

Dislocation

A line in a crystal along which the repeat is out of register, the edge of an extra half-plane of atoms; it moves a row at a time and lets the crystal slip at low stress (Box 5.4). (Chapter 5)

Dispersion

The change of the refractive index with the frequency of the light, which parts colors. (Chapter 11)

Dispersion force

The weak pull between all atoms and molecules from their passing separations of charge, each inducing a matching one in the other: the weak pull between any two atoms or molecules, arising because each one's momentary separation of charge induces a matching one in the other. (The Ladder in Brief; Chapters 1 and 4)

Deoxyribonucleic acid (*DNA*)

The molecule of inheritance. (Chapter 5)

Domain; domain wall

A region of a magnet within which every spin points one way; and the thin layer between two domains in which the spins turn from one direction to the other. (Chapter 8)

Donor

An added atom with one more outer electron than the crystal's atoms, which gives that electron to the conduction band. (Chapter 7)

Doping; dopant

The adding of a small, chosen amount of another element to a semiconductor to set its carriers; and an atom so added. (Chapter 7)

Doublet

A pair of kinds that the weak force turns into each other, such as the up and down quarks, or the electron and its neutrino; the Higgs field has one component for each side. (Chapter 8)

Dulong-Petit law

A warm crystal takes up 3k for each atom and each kelvin, 24.94 joules for each mole and each kelvin. (Chapter 5)

Easy axes

The directions of lowest energy for the alignment of a magnetized crystal. (Chapter 8)

Edge states; surface states

Boundary states in a sheet, along its edge; and in a solid crystal, over its surface. (Chapter 10)

Effective mass

The mass with which an electron in a band answers a push, set by the band's curvature. (Chapter 6)

Effective nuclear charge (Z_{eff})

The true charge Z less the part the electrons between hide: the charge an outer electron finds once part of the nucleus's charge is canceled by the electrons lying between. (Chapter 1)

Einstein's n + 1

The rate of giving out a photon into a state that holds n photons is in proportion to n + 1, and of taking one up in proportion to n (Box 11.3). (Chapter 11)

Electric constant (ε_0)

ε_0, the number that sets, in the international units, how strong a field a given charge makes. (Chapter 4)

Electric potential

The part along time of the field's potential in space and time, whose difference between two places is the voltage between them. (Chapter 9)

Electric quadrupole moment

The measure of how far a body's charge departs from a sphere; the deuteron's is 0.2857 e fm^2 (Puchalski, Komasa and Pachucki, 2020), and a nucleus of spin one half has none. (Chapter 12)

Electrochemical cell

A reaction of oxidation and reduction with its halves set apart, so that its electrons run through an outer circuit, as a current. (Chapter 3)

Electrode

One of a cell's metal strips, at which one half of its reaction takes place: oxidation at the anode and reduction at the cathode. (Chapter 3)

Electromagnetism

The force of electric charge, of light and of every chemical bond. (Chapter 1)

Electron affinity

The energy set free when a neutral atom takes one more electron; largest for the halogens. (Chapter 1)

Electron capture

A proton taking in an electron to become a neutron, with a neutrino sent out; it never happens to a hydrogen atom, which is lighter than a neutron with a neutrino by 0.782 MeV. (Chapters 12 and 13)

Electron spin resonance

The same taking up of photons by unpaired electrons, in a magnetic field, as nuclear magnetic resonance is by nuclei, at 28.02 gigahertz in each tesla. (Chapter 12)

Electron volt (*eV*)

The energy an electron gains in passing through a voltage of one volt; an MeV and a GeV are a million and a thousand million electron volts, a keV a thousand and a TeV a million million. (Preface; The Ladder in Brief; Chapter 1)

Electronic heat capacity

The electrons' share of the energy a metal takes up for each rise of one unit in temperature, in proportion to the temperature, because only electrons within kT of the Fermi level can take up heat. (Chapter 6)

Electrons pressed into protons

In matter squeezed far enough, the electrons at the top of their sea carry more than 0.782 MeV, so electron capture turns protons into neutrons, and exclusion keeps the neutrons from decaying. (Chapter 13)

Energy against kT

The ratio that decides what heat does to a binding or an order: far above one, heat leaves it alone; a few, heat breaks and remakes it; far below one, it is found only by cooling (Box 14.1). (The Ladder in Brief; Chapter 14)

Energy gap (Δ)

In a superconductor, the least energy needed to free one electron from the shared state of pairs, about 1.76 kT_c. (Chapter 9)

Entropy

In everyday words, how disordered a thing is; exactly, the logarithm of the number of a system's microstates with its totals, $S = k \ln W$; it adds for independent systems. (Preface; Chapters 2 and 14)

Equal a priori probabilities

Every microstate with a system's totals counts alike; it follows from the weight the motion keeps and the principle of identity. (Chapter 2)

Equilibrium constant; law of mass action

$K = e^{-\Delta G°/RT}$, the fixed ratio, in balance, of the concentrations of what comes out to those of what goes in, each raised to its number in the reaction (Box 3.2). (Chapter 3)

Equipartition

Each energy that goes as the square of a position or a velocity holds ½kT on average, when kT is large against its quanta. (Chapter 2)

Ergodic hypothesis

The statement that a system's motion passes through every microstate with its energy in time; equal counting holds with the closure that the kept energy gives, whether or not this holds. (Chapter 2)

Evanescent wave

The field reaching a fraction of a wavelength past a surface at which all the light turns back, carrying nothing away. (Chapter 11)

Ewald-Oseen extinction theorem

Inside matter, the waves of the driven electrons cancel the entering wave and build in its place a wave whose phase advances at c/n, every part traveling at c. (Chapter 11)

Exchange; exchange constant

The dependence of the electric push between electrons on their spins, through exclusion; and J, the energy that the exchange gives to aligning two neighboring spins against opposing them, in the energy $-J\ S_1 \cdot S_2$ (Heisenberg). (Chapter 8)

Exchange hole

The region around an electron that another electron with its spin aligned avoids, because their place amplitude changes sign on exchange and vanishes where they coincide. (Chapter 8)

Excitation

A definite amount of energy, with a definite momentum, lifted out of a condensate. (Chapter 9)

Exciton

An electron and a hole bound together by their electric pull, in hydrogen-like levels just below the gap. (Chapter 6)

Exclusion principle

No two fermions of one kind share a state; it follows from the principle of identity; a whole of an odd number of fermions is excluded, a whole of an even number is not (Box 1.2). (Preface; Chapter 1)

Exponent

The power to which e is raised. (Chapters 2 and 3)

Faraday constant

$F = N_A e = 96{,}485.33$ coulombs, the charge of a mole of electrons. (Chapter 3)

Faraday rotation

The turning of the plane of linear polarization by a magnetic field, in any material. (Chapter 11)

Femtometer (fm)

10^{-15} m, about the size of a proton. (The Ladder in Brief; Chapter 1)

Fermi contact interaction

The part of the hyperfine splitting that comes from an S electron's magnet found at the nucleus itself, in proportion to the weight of its state there. (Chapter 12)

Fermi-Dirac and Bose-Einstein distributions

$1/(e^{(\varepsilon - \mu)/kT} + 1)$ and $1/(e^{(\varepsilon - \mu)/kT} - 1)$, the average numbers of fermions and bosons in a state of energy ε (Box 2.5). (Chapter 2)

Fermi energy

For a free-electron metal, the energy of the top of the filled states measured from the bottom of its band, 7.03 eV for copper (Box 6.3). (Chapter 6)

Fermi level

The energy of the top of the filled states of fermions at the lowest temperature; at any temperature, the electrons' chemical potential, the energy at which a state is as likely to be full as empty; in a semiconductor it can lie in the gap. (Chapters 2, 6, 7, 9 and 13)

Fermi sea

The filled states of fermions at the lowest temperature, filled one by one from the lowest. (Chapters 2, 6, 9 and 13)

Fermion

A particle whose spin is an odd number of halves, such as the electron, of which no two of one kind share a state. (Preface; Chapters 1, 2, 13 and 14)

Ferrimagnet

A crystal whose alternating moments are unequal, so that they do not cancel. (Chapter 8)

Ferromagnet

A crystal whose atoms' spins all line up one way. (Chapter 8)

Field

A quantity with a value at every place in space; the field of a force is that force's pull or push at each place. (Chapter 1)

Field-effect transistor; source; drain; gate; threshold

A switch in which a voltage on a gate, through an insulating layer, draws a channel of carriers that joins two regions, the source and the drain; the gate voltage above which the channel forms is the threshold. (Chapter 7)

Field shift

The lifting of the S states by the nucleus's size, in proportion to its mean square radius, largest in heavy atoms. (Chapter 12)

Filling factor (ν)

$\nu = nh/(eB)$, the number of Landau levels the electrons of a sheet fill. (Chapter 10)

Fine structure

The splitting of each energy level into a few close ones that spin-orbit coupling makes, together with the other first corrections from the electron's motion, all of relative order α^2; after every correction from motion hydrogen's levels depend on n and j only (Dirac's formula). (Chapter 1)

Fine-structure constant (α)

α, the strength of electromagnetism, a pure number, 1/137.035999177; in hydrogen's ground state, the electron's speed over the speed of light. (Chapter 1)

First-order change

A change of phase with a jump in energy and entropy, and so a latent heat. (Chapter 4)

Fission

The splitting of a heavy nucleus into lighter ones; it sets energy free, since the binding for each nucleon peaks near iron and nickel. (Chapter 1)

Fluctuations

The small changing departures of a system from its most probable macrostate; their relative size goes as one over the square root of the number of particles. (Chapter 2)

Flux quantum

$h/2e = 2.067833848 \times 10^{-15}$ webers, the flux of one thread round which the pairs' phase winds once. (Chapters 9 and 10)

Forward and reverse bias

A voltage across a junction that lowers its barrier, positive on the p side; and one that raises it. (Chapter 7)

Fourier transform

A calculation that sorts a signal into the frequencies of which it is the sum. (Chapter 12)

Fractional quantum Hall effect

Plateaus of the Hall resistance at fractions of a Landau level, made by the electrons' push. (Chapter 10)

Free-electron model

A metal pictured as fixed ions with a gas of free electrons (Drude), filled as fermions fill their states (Sommerfeld). (Chapter 6)

Free energy

$F = E - TS$, the quantity a system at fixed temperature makes least. (Chapter 2)

Frequency

The number of crests of a wave that pass a point in each second. (Chapter 11)

Fresnel reflection

The share of light sent back at a surface, $((n-1)/(n+1))^2$ straight on, 4 percent at glass. (Chapter 11)

Front

The first part of a change of light to arrive, which travels at c in every material. (Chapter 11)

Fuel cell

An electrochemical cell fed its reacting matter continuously, such as hydrogen and oxygen at 1.23 volts. (Chapter 3)

Fusion

The joining of light nuclei into a heavier one; it sets energy free, since the binding for each nucleon peaks near iron and nickel. (Chapter 1)

g-factor

The ratio of a particle's magnetic moment to the value its angular momentum alone would give, 2 for the electron's spin at lowest order and 1 for orbital motion. (Chapter 1)

Gamma ray

Light of very high energy, given off when a nucleus falls to a lower state. (Chapters 1 and 12)

Gas constant (R)

$R = N_A k = 8.314$ joules for each kelvin and each mole, the Boltzmann constant for a mole. (Chapter 3)

Gauge symmetry

A symmetry whose rotations can be made separately at every place, so that the labels it defines turn with it; the Higgs field's direction in its doublet space is of this kind, and nothing can tell one of its picks from another. (Chapter 8)

Gel

A network of chains or particles reaching through a liquid and holding it in its gaps. (Chapter 4)

Gibbs free energy

G = E + PV − TS, the quantity a system at fixed temperature and pressure makes least. (Chapter 2)

Ginzburg-Landau parameter

The ratio of the penetration depth to the coherence length, which divides type I from type II superconductors at one over the square root of two. (Chapter 9)

Glass; glass transition

A solid whose molecules are caught in the disordered arrangement of a liquid; and the temperature, depending on the rate of cooling, at which a cooling liquid stops flowing and becomes a glass. (The Ladder in Brief; Chapter 4)

Gluon

One of the eight carriers of the strong force. (Chapter 1)

Goldstone boson

The quantum of a wave along a symmetry of the laws that the ground state hides, whose energy falls toward zero as the wave is made longer: among the particles a massless whole of spin zero, as the pions nearly are; in a magnet the magnon, a collective excitation that carries one unit ħ of spin. (Chapter 8)

Graham's law

The leaking of a gas through fine pores at a rate in proportion to its molecules' speed, which at one temperature goes as one over the square root of the mass, by equipartition; the basis of separating isotopes by gaseous diffusion. (Chapter 12)

Grain; grain boundary

One of the many small crystals of a metal or rock; and the surface where two grains, their lattices turned differently, meet. (Chapter 5)

Gravitational waves

Ripples in the shape of space and time that carry energy away. (Chapters 11 and 13)

Ground state

A system's state of least energy, the state with the least of what it can lose; it has nothing further to give up, so it sends nothing out. (The Ladder in Brief; Chapters 1, 8, 12 and 14)

Groups and families

The columns of the periodic table: the alkali metals and the alkaline earth metals, with one and two outer electrons; the halogens, one short of a closed p subshell; the noble gases, with their last subshell closed; the transition metals, lanthanides and actinides, in which an inner subshell fills. The atoms of one column share the arrangement of their valence electrons. (Chapter 1)

Group velocity

The speed of a pulse's envelope. (Chapter 11)

Gyromagnetic ratio (γ)

The ratio γ of a nucleus's moment to its angular momentum. (Chapter 12)

Half-life

The time in which half of a sample has changed; for a collection of radioactive nuclei of mean life τ, $\tau \ln 2$, the time in which half of the collection decays. (Chapters 3 and 12)

Hall effect

The voltage across a strip carrying a current in a magnetic field, whose sign shows the sign of the carriers of charge. (Chapter 6)

Hall conductance

The inverse of the Hall resistance; in a sheet whose filled states wind, a whole number of units of e^2/h. (Chapters 10 and 14)

Hall resistance

The ratio of the voltage across the sheet to the current along it; its inverse is the Hall conductance. (Chapter 10)

Halogens

Group 17 of the periodic table, whose atoms are one electron short of a closed p subshell. (Chapter 1)

Soft and hard magnets

Magnets with a small coercivity and a narrow loop of hysteresis, which follow a field and give it up; and magnets with a large coercivity and a wide loop, which keep their magnetization. (Chapter 8)

Heat

Energy passed because of a difference of temperature, from one system to another. (Chapter 2)

Heat capacity

The energy a system takes up for each rise of one unit in temperature, C = dE/dT. (Chapters 2 and 5)

Heat pump; refrigerator

An engine run backward, using work to carry heat from a colder body to a warmer one: set to warm a house, a heat pump; set to cool a box, a refrigerator. (Chapter 2)

Helium-4; helium-3

Helium of two protons and two neutrons, six particles of spin one half with its electrons; and helium of two protons and one neutron, five. (Chapters 1 and 9)

Higgs boson

The particle of the Higgs field, a field present everywhere in space whose settled value gives the W and Z, the quarks and the charged leptons their masses. (Chapter 1)

Hole

An empty state in a nearly full band, which moves as a positive charge with positive mass; a collective excitation of the band's electrons, apart from the kinds of particle. (Chapter 6)

Hund's first rule

A partly filled subshell fills with spins aligned first, because aligned electrons keep apart, screen each other less and are held more strongly; such atoms are magnets. (Chapter 1)

Hydrogen atom

A single proton with a single electron bound to it, by electromagnetism alone; it carries no net charge. (Chapter 1)

Hydrogen bond

The attraction between a hydrogen atom bound to a strongly electron-pulling atom, such as oxygen, nitrogen or fluorine, and a lone pair of another such atom; stronger than the dispersion force and weaker than a covalent bond. (The Ladder in Brief; Chapter 1)

Hydrogen-like ion

One electron bound to a nucleus of any charge Z; its ground state is Z times smaller than hydrogen's, bound Z^2 times more tightly, with the electron moving at $Z\alpha c$. (Chapter 1)

Hyperfine structure

The splitting of a level by whether the electron's and the proton's spins add (F = 1) or oppose (F = 0). (Chapter 12)

Hysteresis

The lag of a magnet's magnetization behind the field, which makes it depend on the field's history. (Chapter 8)

Ideal gas; ideal gas law

A gas whose molecules are taken as points that exert no force on one another except in a collision; and its law, PV = NkT, or P = nkT (Box 4.1). (Chapter 4)

Impedance of empty space

$Z_0 = \mu_0 c = 376.730313412$ ohms; set against it, the von Klitzing constant gives $R_K/Z_0 = 1/(2\alpha)$. It is the ratio of a light wave's electric field to its magnetic field divided by μ_0, for light traveling through empty space. (Chapter 10)

Incommensuration Theorem

Symmetry and continuity cannot both be simultaneously and fundamentally applied to any event or comparison, nor asymmetry and discontinuity; a structural fact about the nature of knowing. (Chapter 1)

Insulator

A solid whose bands are each full or empty, with a gap above the last full one. (Chapter 6)

Integral

The sum over a continuous range. (Chapter 2)

Integrated circuit

Transistors, diodes and their connections made together in the surface of one chip of silicon. (Chapter 7)

Interference

The adding of waves, which reinforce where they have the same sign and cancel where opposite. (Chapter 1)

Internal conversion

The handing of the energy of a nucleus falling to a lower state to one of the atom's electrons, in place of a gamma ray. (Chapter 12)

Intrinsic semiconductor

A semiconductor conducting by its own lifted electrons alone. (Chapter 6)

Invariant

Whatever stays the same under every change of setting; found as finely as anything can be found, it comes as a countable thing. (Chapter 1)

Ion

An atom or nucleus with a net charge. (The Ladder in Brief; Chapter 1)

Ionic bond

An electron passed over entirely, the two ions held by the electric pull alone, without direction: two ions held together by the electric pull between their opposite charges. (Chapter 1)

Ionization energy

The energy that must be supplied to free an atom's most loosely held electron. (Chapter 1)

Isomer shift; quadrupole splitting; magnetic hyperfine splitting

The three marks of chemistry and magnetism on a Mössbauer line: its move with the density of s electrons at the nucleus, its splitting in two by a changing electric field across the nucleus, and its splitting in six by a magnetic field. (Chapter 12)

Isotope

Different forms of one element, with the same number of protons and different numbers of neutrons; an atom of the same element with a different number of neutrons. (Chapters 1, 3, 9 and 12)

Isotope effect

The fall of a metal's transition temperature, as one over the square root of the nuclear mass, when it is made of heavier isotopes. (Chapter 9)

Josephson junction; DC and AC Josephson effects; Josephson constant

Two superconductors joined through a layer that is not superconducting, about a nanometer thick; a steady (direct) current $I_c \sin \delta$ with no voltage, I_c being the junction's critical current; a current swinging back and forth (alternating) at $2eV/h$ under a voltage V; and the ratio $2e/h$, the same in every material. (Chapter 10)

Kelvin

The unit of temperature on the scale that starts at the lowest temperature there is, with steps the size of the Celsius degree. (Preface; Chapter 2)

Kerr effect

A refractive index changing with the light's strength, in every material. (Chapter 11)

Kind of particle

A species: every particle of one kind is the same as every other, with the same mass, charge and behavior, wherever and whenever it is found; the list of kinds is closed. (Preface; Chapter 1)

Kinetic isotope effect

The slower reaction of a heavier isotope, from its lower zero-point energy and, where tunneling plays a part, from its smaller tunneling. (Chapter 3)

King plot

The comparison of two lines' shifts across several isotopes that takes the mass and field parts apart. (Chapter 12)

Kramers-Kronig relations

Formulas, following from nothing answering before it is driven, that tie a material's index at every frequency to its absorption at every frequency. (Chapter 11)

Kramers' theorem

Reversing time twice reverses an electron's state, so every state has a partner of the same energy and opposite spin. (Chapter 10)

kT

The temperature as an energy, 0.0259 eV at 300 kelvin. (The Ladder in Brief; Chapters 2 and 14)

Ladder of levels

Matter built in levels, quarks into nucleons, nucleons into nuclei, nuclei and electrons into atoms, atoms into molecules, molecules into larger gatherings, each held by what the level below leaves over and each far more weakly than the one below; on the rung of gatherings, molecules and atoms gather into gases, liquids, crystals, metals, magnets, condensates and stars, held by the bonds of single wholes and the feeble pulls between molecules. (Preface; Chapters 1 and 14)

Landau critical velocity

The least ratio of energy to momentum among a condensate's excitations, below which a flow can make none and so loses nothing. (Chapter 9)

Landau level

One of the energies $\hbar\omega_c(n + 1/2)$ of an electron turning in a magnetic field, each with one state for each flux quantum h/e through the sheet. (Chapter 10)

Lanthanides

The first run of the f block, lanthanum to lutetium. (Chapter 1)

Larmor frequency

$f = \gamma B/2\pi$, the frequency at which a nucleus's moment swings round a field B and at which it takes up radio waves, 42.58 megahertz in each tesla for hydrogen. (Chapter 12)

Laser

The device that makes light by light amplification by stimulated emission of radiation, its light of one frequency in one direction, grown in an optical cavity. (Chapter 11)

Lasting and decaying

A particle lasts when it stays as it is unless something strikes it, and it does so when it is the lightest thing that carries the same counts of charge, baryon number and lepton number, all of them together; otherwise, left alone, it decays into lighter particles. (Chapters 1 and 14)

Latent heat

The heat a substance takes in to pass from one phase to another at a fixed temperature and pressure: $L = T\Delta S$. (Chapter 4)

Lattice; unit cell

The set of points, one for each copy of the repeated arrangement, from which a crystal is built; and the smallest block whose copies fill the crystal. (The Ladder in Brief; Chapter 5)

Laughlin state

The state in which every pair of electrons is kept apart as the m-th power of their distance, m odd, filling 1/m of the level (Box 10.3). (Chapter 10)

Light-emitting diode (*LED*)

A junction of a direct-gap semiconductor that, with forward bias, gives out light whose photons carry about the energy of the gap. (Chapter 7)

Lenz's law

A current driven by a changing field makes a field that opposes the change. (Chapter 12)

Lepton

A particle of matter that carries no color. (Chapter 1)

Lepton number

The number of leptons less the number of their antiparticles; every change at the temperatures of the present universe keeps it. (Chapter 1)

Linear (*of the field's laws*)

Any two waves the laws allow, added, make a third, each going on as it would alone; so through the field alone two beams pass through each other unchanged. (Chapter 11)

Liquid crystal; nematic

A phase that flows as a liquid while its rod-like molecules share a direction; and the kind in which they share a direction and nothing else. (Chapter 4)

Liquid-crystal display

A screen setting each region light or dark by turning polarization between two polarizers. (Chapter 11)

Logarithm

The power to which a fixed base must be raised to give the number. (Chapter 2)

Lone pair

A pair of an atom's outer electrons that takes no part in its bonds. (Chapter 1)

Lorentz oscillator model

Each bound electron taken as a charge on a spring with natural frequencies of its own. (Chapter 11)

Lumen

The unit of light as the eye sees it; a lamp's efficiency is counted in lumens for each watt. (Chapter 7)

Macrostate

What is found of a system as a whole, its totals. (Chapter 2)

Madelung's rule

With screening, the subshells fill roughly in order of n + l, and, at a tie, lower n first; it gives periods of 2, 8, 8, 18, 18, 32 and 32. (Chapter 1)

Magic numbers

The numbers of nucleons of one kind, 2, 8, 20, 28, 50, 82 and 126, at which a nuclear shell closes. (Chapter 1)

Magnetic flux; weber

The field times the area it passes through, in webers, one tesla through one square meter. (The Ladder in Brief; Chapter 9)

Magnetic moment

How strong a small magnet a body is, measured by the turning push a magnetic field of a given strength gives it; a charge that goes round has one, and so does the electron's spin; the neutron's, −1.913 nuclear magnetons, shows that it has charged parts. (Chapters 1, 8 and 12)

Magnetic resonance imaging (*MRI*)

Nuclear magnetic resonance turned into pictures of the body, each signal placed by a field that grows along a direction. (Chapter 12)

Magnetization

The magnetic moment of each unit of volume. (Chapter 8)

Magnetocrystalline anisotropy

The dependence of an aligned crystal's energy on the direction of its alignment relative to the crystal's axes, from spin-orbit coupling. (Chapter 8)

Magnetoencephalography

The measuring of the brain's activity by its magnetic fields, with SQUIDs. (Chapter 10)

Magnon

The quantum of a spin wave, a collective excitation that carries one unit ħ of spin, the Goldstone boson of the magnet's hidden symmetry. (Chapter 8)

Majority and minority carriers

The carriers of the kind the doping supplies, and the few of the other kind; their numbers multiply to a product fixed by the temperature. (Chapter 7)

Many-body system

Many particles taken together, with their total energy kept. (Chapter 2)

Maser

An amplifier of microwaves by atoms passing together from an upper level to a lower one. (Chapter 11)

Mass number (A)

The number of nucleons in a nucleus, $A = Z + N$. (The Ladder in Brief; Chapter 1)

Mass shifts, normal and specific

The shift of an atom's levels between isotopes because the nucleus moves a little with its electrons, by about the electron's mass over the nucleus's; and the further part from the correlated motions of many electrons. (Chapter 12)

Matthiessen's rule

The adding of the parts of a metal's resistivity from flaws and from vibrations. (Chapter 6)

Maxwell's four laws

The four laws by which charges and their motion shape the electric and magnetic field, and by which the field changes: a magnetic field has no sources; a magnetic field that changes in time drives an electric field round it (Faraday's law of induction); the electric field spreads out from charge (Gauss's law); and moving charge, together with an electric field that changes in time, drives a magnetic field round it (the Ampère-Maxwell law). They follow from a turn of a charged wave's

phase made separately at each place with a matching change of the potential, from four conditions on any law that fixes the field from the charges, and from a photon that carries no charge. (Chapter 9)

Maxwell's sorter

A device that lets the molecules of a gas pass by what it finds of their motion, the faster one way and the slower the other; it lowers no entropy overall, since it must keep its findings in a memory, and clearing a memory gives off at least kT ln 2 of heat for each bit (Landauer, 1961). (Chapter 2)

Maxwell-Boltzmann distribution

The range of speeds among the molecules of a gas: the Boltzmann factor of each speed's energy, times the v^2 ways of moving at that speed. (Chapter 2)

Mean field

Each spin taken to feel its neighbors only through their average alignment, as a field in proportion to the magnetization (Box 8.2). (Chapter 8)

Megaparsec

About 3.26 million light years, a light year being the distance light travels in a year, about 9.46×10^{15} meters. (Chapter 13)

Meissner effect

A superconductor's pushing of a magnetic field out of itself. (Chapter 9)

Memory

A small system that can stand in any of several states, one for each finding it can keep; a memory of two states keeps one bit. (Chapter 2)

Meson

A whole of a quark and an antiquark. (The Ladder in Brief; Chapter 1)

Metal

A solid whose Fermi level lies inside a band. (Chapter 6)

Metallic bond

The bond in which each atom gives its few loosely held outer electrons to be shared with all its neighbors at once, so the shared electrons move through the whole piece of metal and the bond has no direction. (Chapters 1 and 5)

Metastable state

A state that lasts far longer than those around it because its fast way down is closed. (Chapter 11)

Micelle

A ball of amphiphile molecules in water, tails inward and heads outward. (Chapter 4)

Microstate

One complete arrangement of a system, every particle's state given. (Chapter 2)

Mode

One of the 3N independent ways a crystal of N atoms can vibrate, each a wave of one frequency. (Chapter 5)

Molecule

Atoms held together by bonds. (Preface; Chapter 1)

Momentum

A body's mass times its velocity. (Chapter 1)

Mössbauer effect

The giving off and taking up of gamma rays by nuclei held in a crystal with no energy lost to recoil, the whole crystal taking the momentum when no phonon is made. (Chapter 12)

Mott insulator

A solid whose bands alone would leave a band partly filled, and which holds back the current because its electrons repel one another so strongly that each stays at its own atom. (Chapter 6)

n-type; p-type

A semiconductor whose carriers are mostly electrons from donors; and one whose carriers are mostly holes from acceptors. (Chapter 7)

Natural logarithm

The power to which the base e = 2.718 must be raised to give a number. (Chapter 2)

Natural width

The range $\hbar/\tau$ within which the energy of a state lasting a time τ is defined. (Chapter 12)

Néel temperature

The temperature below which an antiferromagnet's spins alternate. (Chapter 8)

Nernst equation

$E_{cell} = E_{cell}^{\circ} - (RT/(nF))\ \ln Q$, the voltage of a cell at the concentrations it has; zero in balance. (Chapter 3)

Neutrino

A neutral lepton; the neutrino of the electron is the neutral lepton partnered with the electron, of the electron's family. (Chapter 1)

Neutron number (*N*)

The number of a nucleus's neutrons, with A = Z + N. (Chapter 1)

Neutron star

A body about as massive as the Sun, or more, packed to the density of a nucleus and made mostly of neutrons, the collapsed core of a massive star: matter at about the density of a nucleus, mostly neutrons, held up by their exclusion and by the push of the force between nucleons where they are pressed closer than in a nucleus. (Preface; Chapters 1 and 13)

Noble gases

Group 18 of the periodic table, whose atoms have their last subshell closed. (Chapter 1)

Nonlinear optics; second-harmonic generation

Light at frequencies the driving light did not have, from a hold not in proportion to displacement; and light at twice the driving frequency, in crystals with no center of symmetry. (Chapter 11)

Nuclear magnetic resonance (*NMR*)

The taking up of radio waves by nuclei with spin in a magnetic field, at the frequency that matches the difference of energy between neighboring orientations, which is in proportion to the field. (Chapter 12)

Nuclear magneton

$e\hbar/(2m_p)$, the moment of one unit $\hbar$ of orbital angular momentum carried by a charge e with the proton's mass, 1/1836 of the Bohr magneton; the natural unit of a nucleus's magnetic moment. (Chapters 1 and 12)

Nuclear spin, the rule for

A nucleus's spin, its angular momentum in itself, is zero when every nucleon is paired, one half or more with one unpaired nucleon, and usually one or more with one unpaired proton and one unpaired neutron, which can cancel. (Chapters 1 and 12)

Nucleon

A proton or a neutron, the parts of a nucleus. (Preface; Chapter 1)

Nucleus

The atom's small, dense core of protons and neutrons, together called nucleons. (Preface; Chapter 1)

Octahedron

A solid with eight triangular faces and six corners. (Chapter 5)

Ohm's law

The proportion of current to voltage in most solids. (Chapter 6)

Optical activity

The turning of the plane of linear polarization by a chiral material, which slows the two circular polarizations differently. (Chapter 11)

Optical cavity

Two facing mirrors that keep light passing through an inverted material. (Chapter 11)

Optical fiber

A glass thread whose core holds light by total internal reflection. (Chapter 11)

Optics

The study of light and of what matter does to it: its slowing, bending, parting, scattering, polarization and multiplying. (Chapter 11)

Orbital

A state of the electron in an atom, with its shape. (Chapter 1)

Orbital angular momentum

The angular momentum of a particle's motion about a center; for the electron in an atom it comes in whole units of ħ, zero included. (Chapter 1)

Own length

ħ/(mc), the length that a carrier's mass, ħ and c make together, about which its force reaches; inside a superconductor the photon's own length is the penetration depth. (The Ladder in Brief; Chapters 1 and 9)

Oxidation and reduction

The loss and the gain of electrons, a rise and a fall of oxidation state, always together. (Chapter 3)

Oxidation state

The charge an atom would carry if the shared electrons of each of its bonds were given wholly to the atom of the pair that pulls them harder. (Chapter 3)

p-n junction

The boundary inside one crystal between p-type and n-type regions. (Chapter 7)

Paramagnet

A substance whose atoms or molecules keep moments that nothing between them lines up, such as a salt whose metal ions have partly filled subshells, or liquid oxygen; a magnet draws it in, and its magnetization in a field grows as the field and falls as one over the temperature (Curie's law). (Chapter 8)

Particle Data Group

The international collaboration that collects and reviews the measured properties of the particles. (Chapter 1)

Partition function (Z)

Z, the sum of the Boltzmann factors of all a part's states, from which its averages follow. (Chapter 2)

Penetration depth

The depth, $\lambda = (m_e/(\mu_0 n e^2))^{1/2}$ for every electron sharing the phase, over which a magnetic field reaching into a superconductor falls by the factor e (Box 9.3). (Chapter 9)

Phase (*of matter*)

A form of a substance that is the same throughout, with one arrangement of its molecules, meeting another phase of the same substance at a sharp boundary (the sense of Chapter 4, apart from the phase of a wave). (Chapter 4)

Phase (*of a wave*)

The stage of a wave's swing at a place, counted as a fraction of a whole turn (the wave sense, apart from the phases of matter of Chapter 4); a factor that turns a wave's swing forward by a fixed fraction of a turn everywhere changes no finding. (The Ladder in Brief; Chapters 6 and 9)

Phase diagram

The map of the phases of a substance against temperature and pressure (Figure 4.1). (Chapter 4)

Phase velocity

The speed at which a wave's crests move, the wavelength times the frequency. (Chapter 11)

Phonon

A quantum of vibration of a crystal's lattice, a collective excitation; any number of phonons can share a mode, and they stand apart from the kinds of particle; in superfluid helium, the quanta of sound. (The Ladder in Brief; Chapters 5 and 9)

Photodiode; solar cell

A junction that turns light into current, the light making electron-hole pairs that the junction's field carries apart; a solar cell is one made large to gather sunlight for power, turning at most about 30 percent of it into power with one junction. (Chapter 7)

Photon

The particle of light, which carries the electric force between charges. (The Ladder in Brief; Chapter 1)

Picometer (pm)

A millionth of a millionth of a meter. (The Ladder in Brief; Chapter 1)

Piezoelectric effect

The voltage that appears across a crystal with no center of symmetry when it is squeezed, and the flexing a voltage gives it. (Chapter 5)

Pixel

The smallest point of an image; in a camera's sensor, one photodiode. (Chapter 7)

Planck's law

The spectrum of black-body radiation (Box 2.6). (Chapter 2)

Planck mass

$(\hbar c/G)^{1/2}$, 2.18×10^{-8} kilograms, the mass that $\hbar$, c and the constant of gravitation make together. (Chapter 13)

Plasma

A gas in which a large share of the atoms have lost electrons, a mixture of free electrons and ions. (Preface; Chapter 4)

Plasma frequency

$\omega_p = \sqrt{(ne^2/(\varepsilon_0 m_e))}$, the frequency at which a plasma's electrons swing through its ions (Chapter 4); in a metal, $\omega_p = \sqrt{(Ne^2/(\varepsilon_0 m_e))}$, set by the number N of free electrons in each unit of volume, their charge and their mass, below which a metal sends light back and above which it passes it (Chapter 11). (Chapters 4 and 11)

Polar bond

A covalent bond whose shared pair sits nearer one atom than the other. (Chapter 1)

Polarization; linear and circular

The direction of the swing of light's electric field, at right angles to its travel, with two independent polarizations for each direction of travel; chosen as two lines at right angles, or as the field turning clockwise and counterclockwise. (Chapter 11)

Polarizer; wave plate

A sheet passing one linear polarization; and a birefringent plate putting one polarization a quarter cycle behind the other. (Chapter 11)

Polymer; monomer

A molecule made of many small molecules joined end to end into a chain; and each of those small molecules. (Chapter 4)

Population inversion; three- and four-level lasers

More atoms ready to fall than ready to rise, which makes light grow as it passes; and the schemes of levels by which pumping reaches it. (Chapter 11)

Positron

The antiparticle of the electron. (Chapter 1)

Potential

An arrow at each place from which the magnetic field follows, the field through a small loop being how much the potential turns round that loop: the field's potential, whose curl is the magnetic field. (Chapter 9)

Prefactor

The rate of attempts and the counts of states by which the Arrhenius law multiplies its Boltzmann factor (Box 3.1). (Chapter 3)

Pressure; pascal

The force for each unit of area with which a gas or a liquid presses on what holds it; one newton on each square meter, the unit of pressure; the air at sea level presses with the standard atmosphere, 101,325 newtons on each square meter. (Chapters 2 and 13)

Principal quantum number (n)

The number of a level of the atom, $n = n_r + l + 1$, with n_r the number of radial nodes. (Chapter 1)

Principle of identity

What no comparison can distinguish, in any way at all, even in principle, is one thing and not two (*The Quantum Passage*, Chapter 8, Section VI); a difference that no comparison can register is no difference (*Measurement*, Chapter 11, Section IV). (Preface; Chapters 1, 2, 5, 10 and 12)

Proton number (Z)

The number of a nucleus's protons, which is its charge and the atomic number of its element. (Chapter 1)

Pulsar

A spinning neutron star whose beams of radio waves sweep past the Earth at each turn, timed as a clock. (Chapter 13)

Quantized vortex

A thread at whose center the condensate is missing, round which the phase winds whole turns; the flow round it is a whole number of units h/m. (Chapter 9)

Quantum Hall effect

The sheet's Hall resistance on flat plateaus at $h/(\nu e^2)$, with zero resistance along the current, in a sheet of electrons in a strong magnetic field. (The Ladder in Brief; Chapter 10)

Quantum spin Hall effect

The two-dimensional form of a topological insulator, with partners of opposite spin moving opposite ways along each edge. (Chapter 10)

Quark

A particle of matter that carries color, the charge of the strong force. (Preface; Chapter 1)

Quasicrystal

A solid ordered throughout, with sharp diffraction spots, that never repeats, such as one with five-fold symmetry. (Chapter 5)

Radial node

A sphere about the nucleus on which the bound electron's wave is zero. (Chapter 1)

Rayleigh scattering; Mie scattering; Tyndall effect; Raman effect

Scattering by particles small against the wavelength, as the fourth power of the frequency; by particles as large as the wavelength or larger, alike for every color; by colloids, making a beam visible from the side; and with a change of frequency by a molecule's vibration. (Chapter 11)

Reach of a force

The distance over which a force acts; for a carrier of mass m, about its own length $\hbar/(mc)$, the length that its mass, $\hbar$ and c make together; for the massless photon, without bound. (Chapter 1)

Reaction; rate

A change in which molecules rearrange their bonds into other molecules; and how much of it happens in each second. (Chapter 3)

Reciprocal lattice

The lattice of wave vectors whose waves the crystal's repeat fits exactly, whose points are the spots of a diffraction pattern. (Chapter 5)

Recoil energy

$E^2/(2Mc^2)$, the energy a free nucleus of mass M takes in recoil when it gives off a gamma ray of energy E (Box 12.2). (Chapter 12)

Recoil-free fraction

The share of gamma rays given off by nuclei in a crystal with no phonon made, $e^{-E^2\langle x^2\rangle/(\hbar c)^2}$, set by the temperature and the crystal's vibrations. (Chapter 12)

Reduced mass

$m_1m_2/(m_1 + m_2)$ for two particles of masses m_1 and m_2: half a nucleon's mass for two nucleons, and for hydrogen the mass that takes the electron's place when the proton's small motion is counted, the electron's mass made smaller by about one part in 1836, because the proton moves a little too: $m_em_p/(m_e + m_p)$ in hydrogen. (Chapters 1 and 12)

Reduced Planck constant ($\hbar$)

Planck's constant h divided by 2π, $1.054571817... \times 10^{-34}$ joule seconds; the unit in which angular momentum is counted. (Preface; Chapter 1)

Refraction; Snell's law

The bending of light at a surface, toward the side where its phase advances more slowly: $n_1 \sin \theta_1 = n_2 \sin \theta_2$, from the crests matching along the surface. (Chapter 11)

Refractive index (n)

The ratio n of the speed of light c to the speed at which the phase of light advances in a material: 1.333 for water, about 1.5 for glass, 2.417 for diamond. (Chapters 11 and 14)

Relaxation times, longitudinal and transverse

T_1, the time in which tipped nuclear moments return to lie along the field; and T_2, the time in which they fall out of step; the basis of MRI's contrast. (Chapter 12)

Remanence; coercivity

The magnetization a magnet keeps with no field; and the field the other way needed to bring it to zero. (Chapter 8)

Repulsive core

The push between nucleons pressed closer than about half a femtometer. (Chapter 1)

Re-radiated (scattered) waves

The waves a driven charge's swinging sends out at the frequency that drives it: the light given off by charges that a passing wave sets swinging. (Chapter 11)

Residual entropy

The entropy left in a system cooled too fast to reach its ground state; $\ln(3/2)$ for each molecule of ice. (Chapters 2 and 14)

Residual resistivity

The resistivity left at the lowest temperature, from flaws alone. (Chapter 6)

Resistance; resistivity

The ratio of voltage to current; and the resistance of a cube of a material one meter on a side, between opposite faces, 1.678×10^{-8} ohm meters for copper and 7.5×10^{17} for fused quartz. (Chapter 6)

Reversible and irreversible change

A change slow enough that the system stays in balance at every step, which keeps the entropy; and a change too fast for that, which raises it. (Chapter 2)

Rotons

The excitations of superfluid helium near the least energy that its excitations reach at wavelengths about the spacing of its atoms; the quanta of its sound are its phonons. (Chapter 9)

Rydberg energy

$\alpha^2 m_e c^2/2 = 13.606$ eV, the binding of one electron held by a fixed charge of the proton's size; hydrogen's own binding, with the proton's small motion, is 13.598 eV; every bond's energy is a fraction of it. (Chapters 1 and 14)

s, p, d and f states

States with $l = 0$, 1, 2 and 3, whose subshells take 2, 6, 10 and 14 electrons. (Chapter 1)

Saha's rule

$n_e n_p/n_H = (m_e kT/(2\pi\hbar^2))^{3/2} e^{-B/kT}$, the balance of free electrons and bound atoms (Box 2.4). (Chapter 2)

Schwarzschild radius

The radius of the horizon of a mass M, the bound from inside which nothing can leave, $r_s = 2G_N M/c^2$ (*The Gravitational Passage*, Chapter 16, Section III). (Chapter 13)

Screening

The canceling of a charge's field at a distance by charges gathered round it; the charges which gather round a charge and cancel its field at a distance are said to screen it; in an atom, the canceling of part of the nucleus's charge by electrons lying between it and an outer electron. (Chapters 1 and 4)

Second law of thermodynamics

The entropy of an isolated system does not decrease; the traces the particles make of one another, which stay once they have reached many particles, counted. (Chapters 2 and 14)

Second-order Doppler shift

The slowing of a vibrating nucleus's clock by relativity, growing with the temperature, which does not cancel in a line's center. (Chapter 12)

Semiconductor; valence band

An insulator with a gap small enough that heat lifts a few electrons across; and its last full band. (Chapter 6)

Shapiro steps

Voltage steps of hf/2e in a Josephson junction driven by microwaves of frequency f. (Chapter 10)

Shear modulus

A solid's stiffness against sliding one layer over the next. (Chapter 5)

Shell

A set of levels of nearly the same energy with a gap above it, in an atom the states of one n, which take $2n^2$ electrons. (The Ladder in Brief; Chapter 1)

Shielding

The lessening of the field a nucleus meets by the electrons round it, driven round by the field, by the shielding constant σ. (Chapter 12)

Short-range order

The arrangement of a molecule's nearest neighbors, held for a few molecular distances and lost over longer ones, as in a liquid. (Chapter 4)

Silent nuclei

Nuclei with every nucleon paired, such as carbon-12 and oxygen-16, which have spin zero and take up nothing in a magnetic field. (Chapter 12)

Skin depth

The depth, about c/ω_p, to which light below the plasma frequency reaches into a metal. (Chapter 11)

Soft matter

Matter whose structures are large against single molecules and held by weak forces, so that it yields to a gentle push and is reshaped by heat at ordinary temperatures. (Chapter 4)

Space group

The whole set of moves that carry a crystal onto itself, of which there are 230. (Chapter 5)

Spectrum

The light sorted by wavelength; an atom's is a set of sharp lines matching the differences of its levels. (Chapter 1)

Spin

The angular momentum a particle carries in itself, with no motion along a path; the electron's is one half, in units of ħ. (Preface; Chapter 1)

Spin echo

The return of the joint signal of nuclei drifted out of step, when a second pulse reverses the sense of every nucleus's drift; a return found because each trace was held in one nucleus. (Chapter 2)

Spin of a nucleus

The sum of its nucleons' spins and orbital angular momenta, taken as one: zero when every nucleon is paired, an odd number of halves when the mass number is odd, a whole number when both counts are odd (see also Nuclear spin, the rule for). (Chapters 1 and 12)

Spin-orbit coupling

The dependence of a particle's energy on whether its spin and its orbit are aligned ($j = l + 1/2$) or opposed ($j = l - 1/2$): in the nucleus strong, from the strong force, with the aligned level lower; in the atom, the meeting of an electron's spin magnet with the magnetic field it finds, seen from the moving electron itself, from its motion through the electric field around it. (Chapters 1 and 10)

Spin-spin coupling

The splitting of one nucleus's line by the spins of nearby nuclei, through the electrons of the bonds between them, the same in every field. (Chapter 12)

Spin wave

A slow twist of a magnet's held direction running through the crystal; its quantum, a collective excitation that carries one unit ħ of spin, the Goldstone boson of the magnet's hidden symmetry, is the magnon. (Chapter 8)

Spontaneous and stimulated emission

An excited atom giving out a photon with no light present; and giving one out into a state of light in proportion to the photons already in it, the new photon in the same state. (Chapter 11)

Spontaneous symmetry breaking

A symmetry of the laws that the state of least energy does not share: laws the same in every direction, and a ground state that is not; in a magnet the pick can be found, and in the Higgs field's settled value it cannot. (Chapters 8 and 14)

SQUID (*superconducting quantum interference device*)

A superconducting ring with two junctions whose largest current repeats once for each flux quantum, a magnetometer that reads fields of a few femtoteslas. (Chapter 10)

Standard deviation

The typical size of the chance rise and fall of a count. (Chapter 11)

Standard electrode potential

The voltage of a half of a cell against a hydrogen electrode taken as zero, at standard concentrations. (Chapter 3)

Standing wave

A wave whose crests stay in place, made by a wave and its reflection; at the edge of the Brillouin zone two of them, at different energies, bound a gap. (Chapter 6)

State

Everything that can be found of a particle: where it is, how it moves, and which way its spin points. (Preface; Chapter 1)

Statistical mechanics

The physics of many-body systems built by counting their microstates. (Chapter 2)

Stefan-Boltzmann constant; Wien's law

The constant $\sigma = 5.670374419 \times 10^{-8}$ W m^{-2} K^{-4} of the light a black body sends out, σT^4; and the peak wavelength of black-body radiation, $\lambda T = 2.898 \times 10^{-3}$ m K. (Chapter 2)

Stress-energy tensor

The quantity that gives, at each place, the density and the flow of energy and momentum. (Chapter 11)

Strong force

The force that binds quarks, acts only on color, and is carried by eight gluons. (Preface; Chapter 1)

Structure, values and history

Which wholes and orders exist, and the whole numbers they keep, are structure; which last, and where each substance falls, are measured values; how much of each there is, and which allowed state a piece of matter that has not reached its balance keeps, are history. (Preface; Chapters 1 and 14)

Sublimation

The passing of a solid straight into a gas without melting. (Chapter 4)

Subshell

The part of a shell with one value of l, which takes $2(2l + 1)$ electrons, such as 2p or 3d. (Chapter 1)

Superconductor; transition temperature; superconductivity

A metal that carries an electric current with no loss, its electrons bound in pairs; more exactly, a solid that below its transition temperature, T_c, carries a steady current with zero resistance and keeps a magnetic field out of itself; and that state. (The Ladder in Brief; Chapter 9)

Supercooled liquid

A liquid held below its melting point without crystallizing. (Chapter 4)

Supercritical fluid

A substance above its critical point, whose density can be raised smoothly from a gas's to a liquid's with no boiling. (Chapter 4)

Superfluid; two-fluid model; second sound

A liquid that flows without friction because a large share of it is one state; its account as a frictionless superfluid part and a normal part of excitations carrying all the entropy; and a wave of temperature in which the two parts move against each other. (Chapter 9)

Surface tension

The energy it takes to make one more unit of area of a liquid's surface, equal to the pull of the surface along each unit of length; 71.97 thousandths of a joule for each square meter for water at 25 degrees Celsius. (Chapter 4)

Susceptibility

The magnetization a field brings about for each unit of the field, as a pure number, negative for a material pushed away. (Chapter 8)

Temperature

The energy it takes to raise a system's entropy by one unit: $1/T = dS/dE$. (The Ladder in Brief; Chapters 2 and 14)

Tesla

The unit of magnetic field; about one tesla at the face of a strong permanent magnet. (Chapter 8)

Tetrahedron

A solid with four triangular faces. (Chapter 4)

Thermal conductivity

The heat a solid passes each second through each square meter for each kelvin of difference over each meter of length. (Chapter 5)

Thermal wavelength

The length of the wave of a particle moving at a gas's typical speed; a thin gas holds far fewer than one particle in each cube of that side. (Chapter 2)

Thermodynamic arrow of time

The second law as a direction of time: the direction that the count shows. (Chapter 2)

Third law of thermodynamics

At the lowest temperature the entropy is the logarithm of the count of ground states, zero for one. (Chapter 2)

Topological insulator; Z_2 index

A crystal that keeps time reversal with its Z_2 index equal to one, conducting on its boundary while it insulates within; and the two-valued index, zero or one, of a crystal that keeps time reversal. (Chapter 10)

Topological matter

Crystals whose filled bands carry a whole-number winding or a two-valued index that no smooth change keeping the gap can alter, and which therefore carry states at their boundaries. (Chapter 10)

Total internal reflection

The turning back of all the light at a surface, met from inside beyond the critical angle. (Chapter 11)

Transistor

A device in which a small current or voltage at one place switches or controls a much larger current elsewhere. (Chapter 7)

Transition metals

The runs of the d block of the periodic table, the ten columns in which a d subshell fills. (Chapter 1)

Transition state

The arrangement of highest energy that a rearrangement of bonds passes through. (Chapter 3)

Transparent conductor

A solid with a gap wider than visible light and enough free electrons to conduct, with a plasma frequency in the infrared, such as indium tin oxide. (Chapter 6)

Triple point

The one temperature and pressure at which solid, liquid and gas are found together; for water 273.16 kelvin and 611.657 pascals. (Chapter 4)

Tunneling

The passing of a part through a barrier while holding less energy than the barrier, because its wave reaches past the region that confines it; its chance falls as $\exp(-2d\sqrt{(2mV)}/\hbar)$ for a barrier of width d whose top lies an energy V above the energy of a part of mass m (Chapter 3); and, in the words of Chapter 14, a particle's crossing of a barrier with less energy than the barrier, because its wave extends past the region in which it is confined. (Chapters 3 and 14)

Two-dimensional electron gas

A sheet of electrons free to move in two directions and held in the third. (Chapter 10)

Two rules of the kinds

Exclusion, by which no two fermions of one kind share a state and a whole of an odd number of fermions is excluded while one of an even number is not; and angular momentum in whole units of ħ for a path and in halves for spin one half, the whole and half steps of Chapter 1. (Preface; Chapters 1 and 14)

Type I and type II superconductors

Superconductors that keep a field wholly out until a critical field destroys the shared state; and those that let it in as threads between a lower and an upper critical field. (Chapter 9)

Umklapp

A collision of electrons in which the crystal takes up a step of momentum equal to a point of the reciprocal lattice, so that the current is turned back even in a perfect crystal. (Chapter 6)

Uncertainty principle

The narrower the range of places in which a particle can be found, the wider the range of momenta it can be found to have: $\Delta x\, \Delta p \geq \hbar/2$; an instance of the Incommensuration Theorem, true at every scale of size and of energy. (Preface; Chapter 1)

Unitary

Said of a change that keeps the total weight of the possibilities. (Chapter 2)

Universality

The depending of the critical exponents only on the number of dimensions and on the kind of thing that orders, not on the material. (Chapter 8)

Vacancy; interstitial

A lattice place with its atom missing; and an extra atom in a gap between lattice places. (Chapter 5)

Valence

The number of electron-pair bonds an atom forms, the smaller of two numbers, its outer electrons and the electrons it lacks to complete its subshell. (Chapter 1)

Valence electrons

The electrons beyond an atom's last closed subshell, which take part when atoms join. (Chapter 1)

Van der Waals equation

$(P + a/V_m^2)(V_m - b) = RT$, the ideal gas law with the room the molecules fill and their pull put in (Box 4.2). (Chapter 4)

Viscosity

How hard a liquid must be pushed to make it flow at a given speed; it falls steeply as the liquid is warmed. (Chapter 4)

Voltage

The energy each unit of charge gains or gives up between two points, in volts, one volt being one joule for each coulomb of charge. (Chapter 6)

Von Klitzing constant (R_K)

h/e^2 = 25,812.80745... ohms. (Chapter 10)

W and Z bosons

The carriers of the weak force: the W bosons, positive and negative, and the neutral Z boson. (Chapter 1)

Wave vector

An arrow along a wave's travel whose length is 2π over its wavelength. (Chapter 5)

Wavelength

The distance from one crest of a wave to the next. (Chapter 11)

Weak force

The force that turns one kind of quark or lepton into another, carried by the W bosons, positive and negative, and the neutral Z boson. (Chapter 1)

What is new when the wholes are many

No new force: gatherings are held by the bonds of single wholes and the feeble pulls between molecules (the weak pulls of Chapter 1), and their arrangement is decided by the counting of ways at each temperature, with orders of the whole gathering (a repeat, a held direction, a shared phase), collective excitations, and whole numbers kept exactly. (The Ladder in Brief; Chapter 14)

White dwarf

The cooling remnant of a star that has burned its fuel, about as massive as the Sun and about as large as the Earth, held up by its electrons' degeneracy pressure. (The Ladder in Brief; Chapter 13)

Whole and half steps

Orbital angular momentum in whole steps of $\hbar$, zero included, because the angle about a center closes after one turn; spin in half steps for a particle of spin one half, which returns only after two (Box 1.3); the whole units of $\hbar$ and the halves of Chapter 14. (Preface; Chapters 1 and 14)

Wiedemann-Franz law

The ratio of a metal's conduction of heat to its conduction of charge, divided by the temperature, is $(\pi^2/3)(k/e)^2$, the same for every metal whose electrons carry both. (Chapter 6)

Winding

The whole number of times the filled states' phases turn as the crystal momentum is carried over all its values. (Chapter 10)

Work

Energy passed by a force that moves something along its way; it carries no entropy. (Chapter 2)

Work hardening

The stiffening of a metal as it is bent, from its dislocations multiplying and tangling. (Chapter 5)

Zero-point energy

The least energy of a vibration, half a quantum, hf/2, which no cold takes away (Chapter 1); the energy a vibrating bond keeps in its ground state, half a quantum of its vibration (Chapter 3); and, more widely, the energy of motion that a confined particle keeps even in its ground state; for helium it outweighs the gain of packing, so helium stays liquid below about 25 bar (Chapter 5). (Chapters 1, 3 and 5)

Zeroth law; first law

Two systems each in balance with a third are in balance with each other; and the keeping of energy. (Chapter 2)

Zoo

The Story of the Particles, as this book cites it: the book that derives which particles exist, the authority on that question. (Preface; Chapter 1)

Bibliography

Books by the author cited

Landry, Forrest. *An Immanent Metaphysics*. First published 2001. Wytheville, Virginia: UVSM Publications. ISBN 979-8-9896628-4-5. Cited by aphorism number.

Landry, F. (2026). *At the Edge of Reality*; From Black Holes to the Big Bang in Ten Dimensions. Wytheville, Virginia: UVSM Publications. ISBN 979-8-90710-058-9.

Landry, F. (2026). *Incommensuration*; The Theorem and the Three Axioms. Wytheville, Virginia: UVSM Publications. ISBN 979-8-90710-063-3.

Landry, F. (2026). *Measurement*; The Steps from Comparison to Physics. Wytheville, Virginia: UVSM Publications. ISBN 979-8-90710-064-0.

Landry, F. (2026). *The Alphabet of Particles*; Every Particle, Letter and Word, in the Order of Its Derivation. Wytheville, Virginia: UVSM Publications. ISBN 979-8-90710-055-8.

Landry, F. (2026). *The Basis of Physics*; Nineteen Essays on the Structural Limits of Physical Law. Wytheville, Virginia: UVSM Publications. ISBN 979-8-90710-072-5.

Landry, F. (2026). *The Branches of the Kinds*; What the Structure Allows and Forbids. Wytheville, Virginia: UVSM Publications. ISBN 979-8-90710-077-0.

Landry, F. (2026). *The Coming of the Kinds*; How the Particles Came to Be After the Big Bang. Wytheville, Virginia: UVSM Publications. ISBN 979-8-90710-078-7.

Landry, F. (2026). *The Gravitational Passage*; Deriving General Relativity from the Immanent Metaphysics. Wytheville, Virginia: UVSM Publications. ISBN 979-8-90710-056-5.

Landry, F. (2026). *The Kinds of Particle*; Why the Structure Must Be So. Wytheville, Virginia: UVSM Publications. ISBN 979-8-90710-060-2.

Landry, F. (2026). *The Matter We Know*; From the First Atoms to the End of the Periodic Table. Volume One; Wholes. Wytheville, Virginia: UVSM Publications. ISBN 979-8-90710-079-4.

Landry, F. (2026). *The Measures of the Kinds*; The Masses and Mixings of the Particles. Wytheville, Virginia: UVSM Publications. ISBN 979-8-90710-116-6.

Landry, F. (2026). *The Quantum Passage*; Quantum Mechanics from the Structure of Comparison. Wytheville, Virginia: UVSM Publications. ISBN 979-8-90710-073-2.

Landry, F. (2026). *The Story of the Particles*; Why Every Particle Is Required, and Why There Are No More. Wytheville, Virginia: UVSM Publications. ISBN 979-8-90710-053-4. Cited in the text as the zoo.

Landry, F. (2026). *The Strengths of the Kinds*; The Couplings, Their Crossings, and the Scales of the Proton and of Gravity. Wytheville, Virginia: UVSM Publications. ISBN 979-8-90710-115-9.

Other works cited

Abbott, B. P., et al. (LIGO Scientific Collaboration and Virgo Collaboration) (2016). "Observation of Gravitational Waves from a Binary Black Hole Merger". *Physical Review Letters* 116, 061102.

Abbott, B. P., et al. (LIGO Scientific Collaboration and Virgo Collaboration) (2017). "GW170817: Observation of Gravitational Waves from a Binary Neutron Star Inspiral". *Physical Review Letters* 119, 161101.

Abbott, B. P., et al. (LIGO Scientific Collaboration, Virgo Collaboration, Fermi Gamma-ray Burst Monitor and INTEGRAL) (2017). "Gravitational Waves and Gamma-Rays from a Binary Neutron Star Merger: GW170817 and GRB 170817A". *Astrophysical Journal Letters* 848, L13.

Abrikosov, A. A. (1957). "On the Magnetic Properties of Superconductors of the Second Group". *Soviet Physics JETP* 5, 1174.

Aeppli, A., Kim, K., Warfield, W., Safronova, M. S., and Ye, J. (2024). "A clock with 8 $\times 10^{-19}$ systematic uncertainty". *Physical Review Letters* 133, 023401.

Aharonov, Y., and Bohm, D. (1959). "Significance of Electromagnetic Potentials in the Quantum Theory". *Physical Review* 115, 485–491.

Alder, B. J., and Wainwright, T. E. (1957). "Phase Transition for a Hard Sphere System". *Journal of Chemical Physics* 27, 1208.

Allen, J. F., and Misener, A. D. (1938). "Flow of Liquid Helium II". *Nature* 141, 75.

Allred, A. L. (1961). “Electronegativity values from thermochemical data”. *Journal of Inorganic and Nuclear Chemistry* 17, 215–221.

Andersen, T., Haugen, H. K., and Hotop, H. (1999). “Binding Energies in Atomic Negative Ions: III”. *Journal of Physical and Chemical Reference Data* 28, 1511–1533.

Anderson, M. H., Ensher, J. R., Matthews, M. R., Wieman, C. E., and Cornell, E. A. (1995). “Observation of Bose-Einstein Condensation in a Dilute Atomic Vapor”. *Science* 269, 198–201.

Anderson, P. W. (1963). “Plasmons, Gauge Invariance, and Mass”. *Physical Review* 130, 439.

Anderson, P. W., and Rowell, J. M. (1963). “Probable Observation of the Josephson Superconducting Tunneling Effect”. *Physical Review Letters* 10, 230.

Andrews, M. R., Townsend, C. G., Miesner, H.-J., Durfee, D. S., Kurn, D. M., and Ketterle, W. (1997). “Observation of Interference Between Two Bose Condensates”. *Science* 275, 637.

Andrews, T. (1869). “The Bakerian Lecture: On the Continuity of the Gaseous and Liquid States of Matter”. *Philosophical Transactions of the Royal Society of London* 159, 575.

Anthony, T. R., Banholzer, W. F., Fleischer, J. F., Wei, L., Kuo, P. K., Thomas, R. L., and Pryor, R. W. (1990). “Thermal diffusivity of isotopically enriched ^{12}C diamond”. *Physical Review B* 42, 1104.

Appl, M. (1997). “The Haber-Bosch Heritage: The Ammonia Production Technology”. Paper given at the 50th Anniversary of the IFA Technical Conference, Sevilla. www.fertilizer.org.

Apple (2020). “Apple unleashes M1”. Apple Newsroom, 10 November 2020. www.apple.com/newsroom.

Arnold, J. T., Dharmatti, S. S., and Packard, M. E. (1951). “Chemical Effects on Nuclear Induction Signals from Organic Compounds”. *Journal of Chemical Physics* 19, 507.

Arrhenius, S. (1889). “Über die Reaktionsgeschwindigkeit bei der Inversion von Rohrzucker durch Säuren”. *Zeitschrift für physikalische Chemie* 4, 226.

Ashby, N. (2003). “Relativity in the Global Positioning System”. *Living Reviews in Relativity* 6, 1.

Ashcroft, N. W., and Mermin, N. D. (1976). *Solid State Physics*. New York: Holt, Rinehart and Winston.

ATLAS Collaboration (2017). “Evidence for light-by-light scattering in heavy-ion collisions with the ATLAS detector at the LHC”. *Nature Physics* 13, 852.

ATLAS Collaboration (2019). “Observation of light-by-light scattering in ultraperipheral Pb+Pb collisions with the ATLAS detector”. *Physical Review Letters* 123, 052001.

Baber, W. G. (1937). “The contribution to the electrical resistance of metals from collisions between electrons”. *Proceedings of the Royal Society of London A* 158, 383.

Baibich, M. N., Broto, J. M., Fert, A., Nguyen Van Dau, F., Petroff, F., Etienne, P., Creuzet, G., Friederich, A., and Chazelas, J. (1988). “Giant Magnetoresistance of (001)Fe/(001)Cr Magnetic Superlattices”. *Physical Review Letters* 61, 2472.

Bainbridge, K. T., Goldhaber, M., and Wilson, E. (1953). “Influence of the Chemical State on the Lifetime of a Nuclear Isomer, Tc^{99m}”. *Physical Review* 90, 430.

Bardeen, J., and Brattain, W. H. (1948). “The Transistor, a Semi-Conductor Triode”. *Physical Review* 74, 230.

Bardeen, J., Cooper, L. N., and Schrieffer, J. R. (1957). “Theory of Superconductivity”. *Physical Review* 108, 1175.

Barkhausen, H. (1919). “Zwei mit Hilfe der neuen Verstärker entdeckte Erscheinungen”. *Physikalische Zeitschrift* 20, 401.

Bednorz, J. G., and Müller, K. A. (1986). “Possible high T_c superconductivity in the Ba-La-Cu-O system”. *Zeitschrift für Physik B* 64, 189.

Bennett, C. H. (1982). “The thermodynamics of computation—a review”. *International Journal of Theoretical Physics* 21, 905–940.

Beratan, D. N., Betts, J. N., and Onuchic, J. N. (1991). “Protein electron transfer rates set by the bridging secondary and tertiary structure”. *Science* 252, 1285–1288.

Bernevig, B. A., Hughes, T. L., and Zhang, S.-C. (2006). “Quantum Spin Hall Effect and Topological Phase Transition in HgTe Quantum Wells”. *Science* 314, 1757.

Berry, M. V. (1984). “Quantal phase factors accompanying adiabatic changes”. *Proceedings of the Royal Society of London A* 392, 45.

Berry, M. V., and Geim, A. K. (1997). “Of flying frogs and levitrons”. *European Journal of Physics* 18, 307.

Bérut, A., Arakelyan, A., Petrosyan, A., Ciliberto, S., Dillenschneider, R., and Lutz, E. (2012). “Experimental verification of Landauer's principle linking information and thermodynamics”. *Nature* 483, 187–189.

Binasch, G., Grünberg, P., Saurenbach, F., and Zinn, W. (1989). “Enhanced magnetoresistance in layered magnetic structures with antiferromagnetic interlayer exchange”. *Physical Review B* 39, 4828.

Bloch, F. (1928). “Über die Quantenmechanik der Elektronen in Kristallgittern”. *Zeitschrift für Physik* 52, 555.

Bloch, F. (1930). “Zur Theorie des Ferromagnetismus”. *Zeitschrift für Physik* 61, 206.

Bloch, F., Hansen, W. W., and Packard, M. (1946). “Nuclear Induction”. *Physical Review* 69, 127.

Boller, A., Scherrer, H., Schadt, M., and Wild, P. (1972). “Low electrooptic threshold in new liquid crystals”. *Proceedings of the IEEE* 60, 1002–1003.

Boltzmann, L. (1877). “Über die Beziehung zwischen dem zweiten Hauptsatze der mechanischen Wärmetheorie und der Wahrscheinlichkeitsrechnung, respektive den Sätzen über das Wärmegleichgewicht”. *Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften, Mathematisch-Naturwissenschaftliche Classe* 76, Abt. II, 373–435.

Boltzmann, L. (1884). “Ableitung des Stefan'schen Gesetzes, betreffend die Abhängigkeit der Wärmestrahlung von der Temperatur aus der electromagnetischen Lichttheorie”. *Annalen der Physik und Chemie* 258, 291–294.

Bond, H. E., Schaefer, G. H., Gilliland, R. L., Holberg, J. B., Mason, B. D., Lindenblad, I. W., Seitz-McLeese, M., Arnett, W. D., Demarque, P., Spada, F., Young, P. A., Barstow, M. A., Burleigh, M. R., and Gudehus, D. (2017). “The Sirius System and Its Astrophysical Puzzles: Hubble Space Telescope and Ground-based Astrometry”. *Astrophysical Journal* 840, 70.

Born, M., and von Kármán, T. (1912). “Über Schwingungen in Raumgittern”. *Physikalische Zeitschrift* 13, 297.

Bosch, F., et al. (1996). “Observation of Bound-State β^- Decay of Fully Ionized ^{187}Re: ^{187}Re-^{187}Os Cosmochronometry”. *Physical Review Letters* 77, 5190.

Bose, S. N. (1924). “Plancks Gesetz und Lichtquantenhypothese”. *Zeitschrift für Physik* 26, 178–181.

Bothwell, T., Kennedy, C. J., Aeppli, A., Kedar, D., Robinson, J. M., Oelker, E., Staron, A., and Ye, J. (2022). “Resolving the gravitational redshift across a millimetre-scale atomic sample”. *Nature* 602, 420.

Bragg, W. H., and Bragg, W. L. (1913). “The reflection of X-rays by crystals”. *Proceedings of the Royal Society of London A* 88, 428–438.

Bragg, W. L. (1912). “The diffraction of short electromagnetic waves by a crystal”. *Proceedings of the Cambridge Philosophical Society* 17, 43.

Braun, F. (1874). “Ueber die Stromleitung durch Schwefelmetalle”. *Annalen der Physik und Chemie* 153, 556.

Bravais, A. (1850). “Mémoire sur les systèmes formés par des points distribués régulièrement sur un plan ou dans l'espace”. *Journal de l'École Polytechnique* 19, 1.

Brillouin, L. (1914). “Über die Fortpflanzung des Lichtes in dispergierenden Medien”. *Annalen der Physik* 44, 203.

Brillouin, L. (1930). “Les électrons libres dans les métaux et le rôle des réflexions de Bragg”. *Journal de Physique et le Radium* 1, 377.

Cady, W. G. (1922). “The piezo-electric resonator”. *Proceedings of the Institute of Radio Engineers* 10, 83.

Carnot, S. (1824). *Réflexions sur la puissance motrice du feu*. Paris: Bachelier.

Carr, H. Y., and Purcell, E. M. (1954). “Effects of Diffusion on Free Precession in Nuclear Magnetic Resonance Experiments”. *Physical Review* 94, 630.

Chandrasekhar, S. (1931). “The Maximum Mass of Ideal White Dwarfs”. *Astrophysical Journal* 74, 81–82.

Chang, C.-Z., et al. (2013). “Experimental Observation of the Quantum Anomalous Hall Effect in a Magnetic Topological Insulator”. *Science* 340, 167.

Chapin, D. M., Fuller, C. S., and Pearson, G. L. (1954). “A New Silicon p-n Junction Photocell for Converting Solar Radiation into Electrical Power”. *Journal of Applied Physics* 25, 676–677.

Chase, M. W., Jr. (1998). *NIST-JANAF Thermochemical Tables*, 4th edition. *Journal of Physical and Chemical Reference Data*, Monograph 9. Read through the NIST Chemistry WebBook.

Cherenkov, P. A. (1934). “Visible emission of clean liquids by action of γ radiation”. *Doklady Akademii Nauk SSSR* 2, 451.

Clapeyron, É. (1834). “Mémoire sur la puissance motrice de la chaleur”. *Journal de l'École Polytechnique* 14, 153–190.

Clausius, R. (1850). “Ueber die bewegende Kraft der Wärme und die Gesetze, welche sich daraus für die Wärmelehre selbst ableiten lassen”. *Annalen der Physik und Chemie* 79, 368–397 and 500–524.

Cohen, D. (1972). “Magnetoencephalography: Detection of the Brain's Electrical Activity with a Superconducting Magnetometer”. *Science* 175, 664.

Computer History Museum. “1959: Practical Monolithic Integrated Circuit Concept Patented”. The Silicon Engine. www.computerhistory.org.

Computer History Museum. “1960: Metal Oxide Semiconductor (MOS) Transistor Demonstrated”. The Silicon Engine. www.computerhistory.org.

Cooper, L. N. (1956). “Bound Electron Pairs in a Degenerate Fermi Gas”. *Physical Review* 104, 1189.

CRC Handbook of Chemistry and Physics (1981). 62nd edition, Weast, R. C., ed. Boca Raton, Florida: CRC Press.

CRC Handbook of Chemistry and Physics (2004). 84th edition, Lide, D. R., ed. Boca Raton, Florida: CRC Press.

CRC Handbook of Chemistry and Physics (2017). 97th edition, Haynes, W. M., ed.; the properties of ice and water by Harvey, A. H. Boca Raton, Florida: CRC Press.

Croat, J. J., Herbst, J. F., Lee, R. W., and Pinkerton, F. E. (1984). “Pr-Fe and Nd-Fe-based materials: A new class of high-performance permanent magnets”. *Journal of Applied Physics* 55, 2078.

Curie, J., and Curie, P. (1880). “Développement par compression de l'électricité polaire dans les cristaux hémièdres à faces inclinées”. *Bulletin de la Société minéralogique de France* 3, 90.

Curie, P. (1895). “Propriétés magnétiques des corps à diverses températures”. *Annales de Chimie et de Physique* 5, 289.

Daniell, J. F. (1836). “On Voltaic Combinations”. *Philosophical Transactions of the Royal Society of London* 126.

Das, T. R., Reed, C. O., Jr., and Eubank, P. T. (1973). “PVT surface and thermodynamic properties of n-butane”. *Journal of Chemical and Engineering Data* 18, 244–253. Read through the NIST Chemistry WebBook.

Davis, K. B., Mewes, M.-O., Andrews, M. R., van Druten, N. J., Durfee, D. S., Kurn, D. M., and Ketterle, W. (1995). “Bose-Einstein Condensation in a Gas of Sodium Atoms”. *Physical Review Letters* 75, 3969.

de Boer, J. H., and Verwey, E. J. W. (1937). “Semi-conductors with partially and with completely filled 3d-lattice bands”. *Proceedings of the Physical Society* 49 (4S), 59.

de-Picciotto, R., Reznikov, M., Heiblum, M., Umansky, V., Bunin, G., and Mahalu, D. (1997). "Direct observation of a fractional charge". *Nature* 389, 162.

Dean, J. A., ed. (1999). *Lange's Handbook of Chemistry*. 15th edition. New York: McGraw-Hill.

Deaver, B. S., and Fairbank, W. M. (1961). "Experimental Evidence for Quantized Flux in Superconducting Cylinders". *Physical Review Letters* 7, 43.

Debye, P. (1912). "Zur Theorie der spezifischen Wärmen". *Annalen der Physik* 39, 789.

Debye, P., and Hückel, E. (1923). "Zur Theorie der Elektrolyte". *Physikalische Zeitschrift* 24, 185.

Deutsch, J. M. (1991). "Quantum statistical mechanics in a closed system". *Physical Review A* 43, 2046.

Deutsch, M., Förster, E., Hölzer, G., Härtwig, J., Hämäläinen, K., Kao, C.-C., Huotari, S., and Diamant, R. (2004). "X-Ray Spectrometry of Copper: New Results on an Old Subject". *Journal of Research of the National Institute of Standards and Technology* 109, 75.

Dolev, M., Heiblum, M., Umansky, V., Stern, A., and Mahalu, D. (2008). "Observation of a quarter of an electron charge at the $\nu = 5/2$ quantum Hall state". *Nature* 452, 829.

Doll, R., and Näbauer, M. (1961). "Experimental Proof of Magnetic Flux Quantization in a Superconducting Ring". *Physical Review Letters* 7, 51.

Donnelly, R. J., and Barenghi, C. F. (1998). "The Observed Properties of Liquid Helium at the Saturated Vapor Pressure". *Journal of Physical and Chemical Reference Data* 27, 1217.

Drozdov, A. P., Eremets, M. I., Troyan, I. A., Ksenofontov, V., and Shylin, S. I. (2015). "Conventional superconductivity at 203 kelvin at high pressures in the sulfur hydride system". *Nature* 525, 73.

Drude, P. (1900). "Zur Elektronentheorie der Metalle". *Annalen der Physik* 306, 566.

du Trémolet de Lacheisserie, É., Gignoux, D., and Schlenker, M., eds. (2005). *Magnetism: Fundamentals*. New York: Springer.

Dürr, S., Fodor, Z., Frison, J., Hoelbling, C., Hoffmann, R., Katz, S. D., Krieg, S., Kurth, T., Lellouch, L., Lippert, T., Szabo, K. K., and Vulvert, G. (2008). "Ab initio determination of light hadron masses". *Science* 322, 1224.

Dyson, F. J., and Lenard, A. (1967). "Stability of Matter. I". *Journal of Mathematical Physics* 8, 423–434.

Ehrenberg, W., and Siday, R. E. (1949). "The Refractive Index in Electron Optics and the Principles of Dynamics". *Proceedings of the Physical Society B* 62, 8–21.

Ehrenreich, H., and Philipp, H. R. (1962). "Optical Properties of Ag and Cu". *Physical Review* 128, 1622.

Einstein, A. (1905). "Über die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen". *Annalen der Physik* 17, 549.

Einstein, A. (1907). "Die Plancksche Theorie der Strahlung und die Theorie der spezifischen Wärme". *Annalen der Physik* 22, 180–190.

Einstein, A. (1917). "Zur Quantentheorie der Strahlung". *Physikalische Zeitschrift* 18, 121.

Einstein, A., and de Haas, W. J. (1915). "Experimenteller Nachweis der Ampèreschen Molekularströme". *Verhandlungen der Deutschen Physikalischen Gesellschaft* 17, 152.

Eisenstein, J. P., Boebinger, G. S., Pfeiffer, L. N., West, K. W., and He, S. (1992). "New fractional quantum Hall state in double-layer two-dimensional electron systems". *Physical Review Letters* 68, 1383.

EL-CELL GmbH. "What is the nominal voltage of a lithium-ion battery?". www.el-cell.com.

Eliseev, S., Blaum, K., Block, M., Chenmarev, S., Dorrer, H., et al. (2015). "Direct Measurement of the Mass Difference of ^{163}Ho and ^{163}Dy Solves the Q-Value Puzzle for the Neutrino Mass Determination". *Physical Review Letters* 115, 062501.

Elitzur, S. (1975). "Impossibility of spontaneously breaking local symmetries". *Physical Review D* 12, 3978–3982.

Emery, G. T. (1972). "Perturbation of Nuclear Decay Rates". *Annual Review of Nuclear Science* 22, 165–202.

Engineering ToolBox. "Water Density, Specific Weight and Thermal Expansion Coefficients: Temperature and Pressure Dependence". www.engineeringtoolbox.com.

Epstein, S., Buchsbaum, R., Lowenstam, H. A., and Urey, H. C. (1953). "Revised carbonate-water isotopic temperature scale". *Geological Society of America Bulletin* 64, 1315.

Erisman, J. W., Sutton, M. A., Galloway, J., Klimont, Z., and Winiwarter, W. (2008). "How a century of ammonia synthesis changed the world". *Nature Geoscience* 1, 636–639.

Essmann, U., and Träuble, H. (1967). "The direct observation of individual flux lines in type II superconductors". *Physics Letters A* 24, 526.

Euler, H., and Heisenberg, W. (1936). "Folgerungen aus der Diracschen Theorie des Positrons". *Zeitschrift für Physik* 98, 714.

European Committee for Standardization. EN 10088-1, *Stainless steels: List of stainless steels*. Read through a secondary page.

Ewald, P. P. (1912). *Dispersion und Doppelbrechung von Elektronengittern* (*Kristallen*). Doctoral dissertation, Munich.

Eyring, H. (1935). "The Activated Complex in Chemical Reactions". *Journal of Chemical Physics* 3, 107–115.

Fedorov, E. S. (1891). *The Symmetry of Regular Systems of Figures* (in Russian). St. Petersburg. In English: Fedorov, E. S. (1971). *Symmetry of Crystals*. American Crystallographic Association Monograph 7.

Fermi, E. (1926). "Zur Quantelung des idealen einatomigen Gases". *Zeitschrift für Physik* 36, 902–912.

Fermi, E. (1930). "Über die magnetischen Momente der Atomkerne". *Zeitschrift für Physik* 60, 320.

Feynman, R. P. (1955). "Application of Quantum Mechanics to Liquid Helium". *Progress in Low Temperature Physics* 1, 17.

Feynman, R. P., Leighton, R. B., and Sands, M. (1963). *The Feynman Lectures on Physics*, Volume I. Reading, Massachusetts: Addison-Wesley.

Feynman, R. P., Leighton, R. B., and Sands, M. (1964). *The Feynman Lectures on Physics*, Volume II. Reading, Massachusetts: Addison-Wesley.

File, J., and Mills, R. G. (1963). "Observation of Persistent Current in a Superconducting Solenoid". *Physical Review Letters* 10, 93.

Fixsen, D. J. (2009). "The Temperature of the Cosmic Microwave Background". *Astrophysical Journal* 707, 916.

Fixsen, D. J., Cheng, E. S., Gales, J. M., Mather, J. C., Shafer, R. A., and Wright, E. L. (1996). “The Cosmic Microwave Background Spectrum from the Full COBE FIRAS Data Set”. *Astrophysical Journal* 473, 576.

Flory, P. J. (1953). *Principles of Polymer Chemistry*. Ithaca, New York: Cornell University Press.

Fonseca, E., et al. (2021). “Refined Mass and Geometric Measurements of the High-mass PSR J0740+6620”. *Astrophysical Journal Letters* 915, L12.

Foucault, L. (1850). “Méthode générale pour mesurer la vitesse de la lumière dans l'air et les milieux transparents”. *Comptes Rendus de l'Académie des Sciences* 30, 551.

Fowler, R. H. (1926). “On Dense Matter”. *Monthly Notices of the Royal Astronomical Society* 87, 114.

Frank, I. M., and Tamm, I. E. (1937). “Coherent visible radiation of fast electrons passing through matter”. *Doklady Akademii Nauk SSSR* 14, 109.

Franken, P. A., Hill, A. E., Peters, C. W., and Weinreich, G. (1961). “Generation of Optical Harmonics”. *Physical Review Letters* 7, 118.

Franklin, R. E., and Gosling, R. G. (1953). “Molecular Configuration in Sodium Thymonucleate”. *Nature* 171, 740–741.

Franz, R., and Wiedemann, G. (1853). “Ueber die Wärme-Leitungsfähigkeit der Metalle”. *Annalen der Physik* 165, 497.

Frenkel, J. (1926). “Zur Theorie der Elastizitätsgrenze und der Festigkeit kristallinischer Körper”. *Zeitschrift für Physik* 37, 572.

Fresnel, A.-J. (1823). “Mémoire sur la loi des modifications que la réflexion imprime à la lumière polarisée”. Read to the Académie des Sciences in 1823; *Mémoires de l'Académie des Sciences* 11, 393 (1832).

Friedrich, W., Knipping, P., and Laue, M. (1912). “Interferenz-Erscheinungen bei Röntgenstrahlen”. *Sitzungsberichte der Königlich Bayerischen Akademie der Wissenschaften*, 303.

Fröhlich, H. (1950). “Theory of the Superconducting State. I. The Ground State at the Absolute Zero of Temperature”. *Physical Review* 79, 845.

Gamow, G. (1928). “Zur Quantentheorie des Atomkernes”. *Zeitschrift für Physik* 51, 204–212.

German Aerospace Center (DLR), Ionosphere Monitoring and Prediction Center. "NmF2 Model". impc.dlr.de.

Giaever, I. (1960). "Energy Gap in Superconductors Measured by Electron Tunneling". *Physical Review Letters* 5, 147.

Giauque, W. F., and Stout, J. W. (1936). "The Entropy of Water and the Third Law of Thermodynamics. The Heat Capacity of Ice from 15 to 273°K". *Journal of the American Chemical Society* 58, 1144.

Gibbs, J. W. (1902). *Elementary Principles in Statistical Mechanics*. New York: Charles Scribner's Sons.

Ginzburg, V. L., and Landau, L. D. (1950). "On the Theory of Superconductivity". *Zhurnal Eksperimental'noi i Teoreticheskoi Fiziki* 20, 1064.

Goldstein, S., Lebowitz, J. L., Tumulka, R., and Zanghì, N. (2006). "Canonical Typicality". *Physical Review Letters* 96, 050403.

Gordon, J. P., Zeiger, H. J., and Townes, C. H. (1954). "Molecular Microwave Oscillator and New Hyperfine Structure in the Microwave Spectrum of NH_3". *Physical Review* 95, 282.

Gough, C. E., et al. (1987). "Flux quantization in a high-T_c superconductor". *Nature* 326, 855.

Greenwood, N. N., and Earnshaw, A. (1997). *Chemistry of the Elements*. Oxford: Butterworth-Heinemann.

Greywall, D. S. (1986). "^{3}He specific heat and thermometry at millikelvin temperatures". *Physical Review B* 33, 7520.

Grisenti, R. E., Schöllkopf, W., Toennies, J. P., Hegerfeldt, G. C., Köhler, T., and Stoll, M. (2000). "Determination of the Bond Length and Binding Energy of the Helium Dimer by Diffraction from a Transmission Grating". *Physical Review Letters* 85, 2284.

Hahn, E. L. (1950). "Spin Echoes". *Physical Review* 80, 580.

Haldane, F. D. M. (1988). "Model for a Quantum Hall Effect without Landau Levels: Condensed-Matter Realization of the 'Parity Anomaly'". *Physical Review Letters* 61, 2015.

Hall, C. M. (1889). "Process of reducing aluminium from its fluoride salts by electrolysis". US Patent 400,664, 2 April 1889.

Hall, E. H. (1879). "On a New Action of the Magnet on Electric Currents". *American Journal of Mathematics* 2, 287–292.

Hall, E. O. (1951). "The Deformation and Ageing of Mild Steel: III Discussion of Results". *Proceedings of the Physical Society B* 64, 747.

Hall, H. E., and Vinen, W. F. (1956). "The rotation of liquid helium II. I. Experiments on the propagation of second sound in uniformly rotating helium II". *Proceedings of the Royal Society of London A* 238, 204–214.

Hall, R. N., Fenner, G. E., Kingsley, J. D., Soltys, T. J., and Carlson, R. O. (1962). "Coherent Light Emission From GaAs Junctions". *Physical Review Letters* 9, 366.

Halperin, B. I. (1982). "Quantized Hall conductance, current-carrying edge states, and the existence of extended states in a two-dimensional disordered potential". *Physical Review B* 25, 2185.

Halperin, B. I. (1983). "Theory of the quantized Hall conductance". *Helvetica Physica Acta* 56, 75.

Halperin, B. I., Lee, P. A., and Read, N. (1993). "Theory of the half-filled Landau level". *Physical Review B* 47, 7312.

Hardy, J. C., and Towner, I. S. (2020). "Superallowed $0^+ \to 0^+$ nuclear β decays: 2020 critical survey, with implications for V_{ud} and CKM unitarity". *Physical Review C* 102, 045501.

Heisenberg, W. (1928). "Zur Theorie des Ferromagnetismus". *Zeitschrift für Physik* 49, 619.

Hellwig, H., Vessot, R. F. C., Levine, M. W., Zitzewitz, P. W., Allan, D. W., and Glaze, D. J. (1970). "Measurement of the Unperturbed Hydrogen Hyperfine Transition Frequency". *IEEE Transactions on Instrumentation and Measurement* IM-19, 200.

Hewish, A., Bell, S. J., Pilkington, J. D. H., Scott, P. F., and Collins, R. A. (1968). "Observation of a Rapidly Pulsating Radio Source". *Nature* 217, 709.

Holonyak, N., and Bevacqua, S. F. (1962). "Coherent (visible) light emission from $Ga(As_{1-x}P_x)$ junctions". *Applied Physics Letters* 1, 82.

Hoover, W. G., and Ree, F. H. (1968). "Melting transition and communal entropy for hard spheres". *Journal of Chemical Physics* 49, 3609–3617.

Hsieh, D., Qian, D., Wray, L., Xia, Y., Hor, Y. S., Cava, R. J., and Hasan, M. Z. (2008). "A topological Dirac insulator in a quantum spin Hall phase". *Nature* 452, 970.

Huber, K. P., and Herzberg, G. (1979). *Constants of Diatomic Molecules* (*Molecular Spectra and Molecular Structure* IV). New York: Van Nostrand Reinhold.

Hughes, D. S., and Eckart, C. (1930). "The Effect of the Motion of the Nucleus on the Spectra of Li I and Li II". *Physical Review* 36, 694.

Hulse, R. A., and Taylor, J. H. (1975). "Discovery of a pulsar in a binary system". *Astrophysical Journal* 195, L51.

International Association for the Properties of Water and Steam (1992). "Revised Supplementary Release on Saturation Properties of Ordinary Water Substance", SR1-86(1992). www.iapws.org.

International Association for the Properties of Water and Steam (2008). "Revised Release on the Pressure along the Melting and Sublimation Curves of Ordinary Water Substance". www.iapws.org.

International Association for the Properties of Water and Steam (2014). "Revised Release on the Surface Tension of Ordinary Water Substance", R1-76(2014). www.iapws.org.

International Astronomical Union (2015). Resolution B3, "On recommended nominal conversion constants for selected solar and planetary properties". Published in Prša, A., et al. (2016). "Nominal Values for Selected Solar and Planetary Quantities: IAU 2015 Resolution B3". *Astronomical Journal* 152, 41.

International Bureau of Weights and Measures (2019). *The International System of Units* (*SI*). 9th edition. Sèvres: Bureau International des Poids et Mesures. With its pages on the defining constants and on the definition of the second, www.bipm.org.

International Bureau of Weights and Measures. "Redefinition of the second". www.bipm.org.

International Electrotechnical Commission. IEC 60908, *Audio recording: Compact disc digital audio system* (the Red Book). Read through a secondary page.

International Union of Pure and Applied Chemistry. *Compendium of Chemical Terminology*, the entry "colloidal". goldbook.iupac.org.

International Union of Pure and Applied Chemistry. Teaching material on the catalytic converter. old.iupac.org.

ITER Organization. "External heating systems". www.iter.org.

Jain, J. K. (1989). "Composite-fermion approach for the fractional quantum Hall effect". *Physical Review Letters* 63, 199.

Jaklevic, R. C., Lambe, J., Silver, A. H., and Mercereau, J. E. (1964). "Quantum Interference Effects in Josephson Tunneling". *Physical Review Letters* 12, 159.

Janssen, L. P. B. M., and Warmoeskerken, M. M. C. G. (2006). *Transport Phenomena Data Companion*. Delft: VSSD.

Janssen, T. J. B. M., Fletcher, N. E., Goebel, R., Williams, J. M., Tzalenchuk, A., Yakimova, R., Kubatkin, S., Lara-Avila, S., and Falko, V. I. (2012). "Precision comparison of the quantum Hall effect in graphene and gallium arsenide". *Metrologia* 49, 294.

Javan, A., Bennett, W. R., and Herriott, D. R. (1961). "Population Inversion and Continuous Optical Maser Oscillation in a Gas Discharge Containing a He-Ne Mixture". *Physical Review Letters* 6, 106.

Johnson, R. D., III (2022). *NIST Computational Chemistry Comparison and Benchmark Database*, NIST Standard Reference Database 101, Release 22. Gaithersburg, Maryland: National Institute of Standards and Technology.

Josephson, B. D. (1962). "Possible new effects in superconductive tunnelling". *Physics Letters* 1, 251.

Joyce, S. R. G., Barstow, M. A., Holberg, J. B., Bond, H. E., Casewell, S. L., and Burleigh, M. R. (2018). "The gravitational redshift of Sirius B". *Monthly Notices of the Royal Astronomical Society* 481, 2361.

Jung, M., et al. (1992). "First observation of bound-state β^- decay". *Physical Review Letters* 69, 2164.

Kamerlingh Onnes, H. (1911). "The resistance of pure mercury at helium temperatures". *Communications from the Physical Laboratory of the University of Leiden* 120b.

Kamihara, Y., Watanabe, T., Hirano, M., and Hosono, H. (2008). "Iron-Based Layered Superconductor $La[O_{1-x}F_x]FeAs$ ($x = 0.05$–0.12) with $T_c = 26$ K". *Journal of the American Chemical Society* 130, 3296.

Kane, C. L., and Mele, E. J. (2005). "Z_2 Topological Order and the Quantum Spin Hall Effect". *Physical Review Letters* 95, 146802; and "Quantum Spin Hall Effect in Graphene". *Physical Review Letters* 95, 226801.

Kao, K. C., and Hockham, G. A. (1966). "Dielectric-fibre surface waveguides for optical frequencies". *Proceedings of the Institution of Electrical Engineers* 113, 1151.

Kapitza, P. (1938). "Viscosity of Liquid Helium below the λ-Point". *Nature* 141, 74.

Kazimierczuk, T., Fröhlich, D., Scheel, S., Stolz, H., and Bayer, M. (2014). "Giant Rydberg excitons in the copper oxide Cu_2O". *Nature* 514, 343.

Kim, H., Gilmore, C. M., Piqué, A., Horwitz, J. S., Mattoussi, H., Murata, H., Kafafi, Z. H., and Chrisey, D. B. (1999). "Electrical, optical, and structural properties of indium-tin-oxide thin films for organic light-emitting devices". *Journal of Applied Physics* 86, 6451.

King, W. H. (1963). "Comments on the Article 'Peculiarities of the Isotope Shift in the Samarium Spectrum'". *Journal of the Optical Society of America* 53, 638–639.

Kittel, C. (1996). *Introduction to Solid State Physics*. New York: Wiley.

Kittel, C. (2005). *Introduction to Solid State Physics*. Hoboken, New Jersey: Wiley.

König, M., Wiedmann, S., Brüne, C., Roth, A., Buhmann, H., Molenkamp, L. W., Qi, X.-L., and Zhang, S.-C. (2007). "Quantum Spin Hall Insulator State in HgTe Quantum Wells". *Science* 318, 766.

Kramers, H. A. (1930). "Théorie générale de la rotation paramagnétique dans les cristaux". *Proceedings of the Royal Academy of Sciences at Amsterdam* 33, 959.

Kramida, A., Ralchenko, Yu., Reader, J., and NIST ASD Team (2024). *NIST Atomic Spectra Database*. Gaithersburg, Maryland: National Institute of Standards and Technology.

Krane, K. S. (1987). *Introductory Nuclear Physics*. New York: Wiley.

Kwan, A., Dudley, J., and Lantz, E. (2002). "Who really discovered Snell's law?". *Physics World* 15 (4), 64.

Lamb, W. E. (1939). "Capture of Neutrons by Atoms in a Crystal". *Physical Review* 55, 190.

Lamb, W. E. (1941). "Internal Diamagnetic Fields". *Physical Review* 60, 817.

Lamptech. "Fluorescent Lamp Operation". www.lamptech.co.uk.

Landau, L. (1930). "Diamagnetismus der Metalle". *Zeitschrift für Physik* 64, 629.

Landau, L. D. (1941). "Theory of the Superfluidity of Helium II". *Journal of Physics USSR* 5, 71.

Landau, L., and Pomeranchuk, I. (1936). *Zhurnal Eksperimental'noi i Teoreticheskoi Fiziki* 7, 379.

Landauer, R. (1961). "Irreversibility and Heat Generation in the Computing Process". *IBM Journal of Research and Development* 5, 183–191.

Langmuir, I. (1928). "Oscillations in Ionized Gases". *Proceedings of the National Academy of Sciences* 14, 627.

Laughlin, R. B. (1981). "Quantized Hall conductivity in two dimensions". *Physical Review B* 23, 5632.

Laughlin, R. B. (1983). "Anomalous Quantum Hall Effect: An Incompressible Quantum Fluid with Fractionally Charged Excitations". *Physical Review Letters* 50, 1395.

LightPath Technologies. "What is Long Wave Infrared Technology?". www.lightpath.com.

Lisiecki, L. E., and Raymo, M. E. (2005). "A Pliocene-Pleistocene stack of 57 globally distributed benthic $\delta^{18}O$ records". *Paleoceanography* 20, PA1003.

Liu, J., Salumbides, E. J., Hollenstein, U., Koelemeij, J. C. J., Eikema, K. S. E., Ubachs, W., and Merkt, F. (2009). "Determination of the ionization and dissociation energies of the hydrogen molecule". *Journal of Chemical Physics* 130, 174306.

Liu, J., Sprecher, D., Jungen, C., Ubachs, W., and Merkt, F. (2010). "Determination of the ionization and dissociation energies of the deuterium molecule (D_2)". *Journal of Chemical Physics* 132, 154301.

London, F. (1938). "The λ-Phenomenon of Liquid Helium and the Bose-Einstein Degeneracy". *Nature* 141, 643.

London, F., and London, H. (1935). "The Electromagnetic Equations of the Supraconductor". *Proceedings of the Royal Society of London A* 149, 71.

Los Alamos National Laboratory. "Sodium". *Periodic Table of Elements*. periodic.lanl.gov.

Maiman, T. H. (1960). "Stimulated Optical Radiation in Ruby". *Nature* 187, 493.

Matthiessen, A., and Vogt, C. (1864). "On the Influence of Temperature on the Electric Conducting-Power of Alloys". *Philosophical Transactions of the Royal Society of London* 154, 167.

Maxwell, E. (1950). "Isotope Effect in the Superconductivity of Mercury". *Physical Review* 78, 477.

Maxwell, J. C. (1860). "Illustrations of the dynamical theory of gases". *Philosophical Magazine* 19, 19–32.

Maxwell, J. C. (1865). "A Dynamical Theory of the Electromagnetic Field". *Philosophical Transactions of the Royal Society of London* 155, 459–512.

Maxwell, J. C. (1871). *Theory of Heat*. London: Longmans, Green, and Co.

Meissner, W., and Ochsenfeld, R. (1933). “Ein neuer Effekt bei Eintritt der Supraleitfähigkeit”. *Die Naturwissenschaften* 21, 787.

Mendeleev, D. (1869). “Über die Beziehungen der Eigenschaften zu den Atomgewichten der Elemente”. *Zeitschrift für Chemie* 12, 405–406.

Mie, G. (1908). “Beiträge zur Optik trüber Medien, speziell kolloidaler Metallösungen”. *Annalen der Physik* 330, 377.

Miller, B. G., Hassell, A. M., Wolfenden, R., Milburn, M. V., and Short, S. A. (2000). “Anatomy of a proficient enzyme: The structure of orotidine 5′-monophosphate decarboxylase in the presence and absence of a potential transition state analog”. *Proceedings of the National Academy of Sciences* 97, 2011–2016.

Miller, M. C., et al. (2021). “The Radius of PSR J0740+6620 from NICER and XMM-Newton Data”. *Astrophysical Journal Letters* 918, L28.

Mohr, P. J., Newell, D. B., Taylor, B. N., and Tiesinga, E. (2025). “CODATA recommended values of the fundamental physical constants: 2022”. *Reviews of Modern Physics* 97, 025002. Cited in the text as CODATA 2022.

Moon, P. B. (1951). “Resonant nuclear scattering of gamma-rays: theory and preliminary experiments”. *Proceedings of the Physical Society A* 64, 76.

Moore, G., and Read, N. (1991). “Nonabelions in the fractional quantum Hall effect”. *Nuclear Physics B* 360, 362.

Mössbauer, R. L. (1958). “Kernresonanzfluoreszenz von Gammastrahlung in Ir^{191}”. *Zeitschrift für Physik* 151, 124.

Mott, N. F. (1949). “The basis of the electron theory of metals, with special reference to the transition metals”. *Proceedings of the Physical Society A* 62, 416–422.

Mukerjee, P., and Mysels, K. J. (1971). *Critical Micelle Concentrations of Aqueous Surfactant Systems*. NSRDS-NBS 36. Washington: National Bureau of Standards.

Nagamatsu, J., Nakagawa, N., Muranaka, T., Zenitani, Y., and Akimitsu, J. (2001). “Superconductivity at 39 K in magnesium diboride”. *Nature* 410, 63.

NANOGrav Collaboration: Agazie, G., et al. (2023). “The NANOGrav 15 yr Data Set: Evidence for a Gravitational-wave Background”. *Astrophysical Journal Letters* 951, L8.

Nassau, K. (1983). *The Physics and Chemistry of Color*. New York: Wiley.

National Institute of Standards and Technology. *Atomic Weights and Isotopic Compositions for All Elements*. physics.nist.gov. Its masses are those of Wang, M., et al. (2012), "The AME2012 atomic mass evaluation", *Chinese Physics C* 36, 1603.

National Institute of Standards and Technology. *NIST Chemistry WebBook*, NIST Standard Reference Database 69, the entry for methane, as collected by Cheméo, www.chemeo.com.

Néel, L. (1948). "Propriétés magnétiques des ferrites; ferrimagnétisme et antiferromagnétisme". *Annales de Physique* 3, 137.

Nernst, W. (1906). "Ueber die Berechnung chemischer Gleichgewichte aus thermischen Messungen". *Nachrichten von der Königlichen Gesellschaft der Wissenschaften zu Göttingen, Mathematisch-physikalische Klasse* 1906, 1.

NETZSCH. "PET: Polyethylene terephthalate". Polymer database. analyzing-testing.netzsch.com.

Newton, I. (1672). "A Letter of Mr. Isaac Newton, Professor of the Mathematicks in the University of Cambridge; containing his New Theory about Light and Colors". *Philosophical Transactions of the Royal Society* 6, 3075–3087.

Nobel Foundation (1956). The Nobel Prize in Physics 1956, summary. www.nobelprize.org.

Nobel Foundation (1970). The Nobel Prize in Physics 1970, Louis Néel, facts. www.nobelprize.org.

Nobel Foundation (2009). The Nobel Prize in Physics 2009, press release. www.nobelprize.org.

Nobel Foundation (2014). The Nobel Prize in Physics 2014, press release. www.nobelprize.org.

Noether, E. (1918). "Invariante Variationsprobleme". *Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen, Mathematisch-Physikalische Klasse*, 235.

Novoselov, K. S., et al. (2007). "Room-Temperature Quantum Hall Effect in Graphene". *Science* 315, 1379.

Ohm, G. S. (1827). *Die galvanische Kette, mathematisch bearbeitet*. Berlin: Riemann.

Ohtsuki, T., Yuki, H., Muto, M., Kasagi, J., and Ohno, K. (2004). "Enhanced Electron-Capture Decay Rate of ^{7}Be Encapsulated in C_{60} Cages". *Physical Review Letters* 93, 112501.

Onsager, L. (1944). “Crystal Statistics. I. A Two-Dimensional Model with an Order-Disorder Transition”. *Physical Review* 65, 117.

Onsager, L. (1949). Discussion on statistical hydrodynamics. *Il Nuovo Cimento* 6, Supplement 2, 279.

Orowan, E. (1934). “Zur Kristallplastizität”. *Zeitschrift für Physik* 89, 634.

Oseen, C. W. (1915). “Über die Wechselwirkung zwischen zwei elektrischen Dipolen und über die Drehung der Polarisationsebene in Kristallen und Flüssigkeiten”. *Annalen der Physik* 48, 1.

Osheroff, D. D., Richardson, R. C., and Lee, D. M. (1972). “Evidence for a New Phase of Solid He^3”. *Physical Review Letters* 28, 885.

Particle Data Group: Navas, S., et al. (2024). “Review of Particle Physics”. *Physical Review D* 110, 030001.

Particle Data Group: Takahashi, F., et al. (2026). “Review of Particle Physics”. *International Journal of Modern Physics A* 41, 2630011. With its online listings, pdgLive.

Pasteur, L. (1848). “Sur les relations qui peuvent exister entre la forme cristalline, la composition chimique et le sens de la polarisation rotatoire”. *Annales de Chimie et de Physique* 24, 442.

Pauli, W. (1925). “Über den Zusammenhang des Abschlusses der Elektronengruppen im Atom mit der Komplexstruktur der Spektren”. *Zeitschrift für Physik* 31, 765–783.

Pauli, W. (1940). “The Connection Between Spin and Statistics”. *Physical Review* 58, 716.

Pauling, L. (1935). “The Structure and Entropy of Ice and of Other Crystals with Some Randomness of Atomic Arrangement”. *Journal of the American Chemical Society* 57, 2680.

Peierls, R. (1929). “Zur kinetischen Theorie der Wärmeleitung in Kristallen”. *Annalen der Physik* 395, 1055.

Peierls, R. E. (1955). *Quantum Theory of Solids*. Oxford: Clarendon Press.

Penrose, R. (1974). “The role of aesthetics in pure and applied mathematical research”. *Bulletin of the Institute of Mathematics and its Applications* 10, 266.

Perrin, J. (1909). “Mouvement brownien et réalité moléculaire”. *Annales de Chimie et de Physique*, 8th series, 18, 5–114.

Peshkov, V. (1944). “‘Second Sound’ in Helium II”. *Journal of Physics USSR* 8, 381.

Petch, N. J. (1953). “The Cleavage Strength of Polycrystals”. *Journal of the Iron and Steel Institute* 174, 25.

Petit, A.-T., and Dulong, P.-L. (1819). “Recherches sur quelques points importants de la Théorie de la Chaleur”. *Annales de Chimie et de Physique* 10, 395.

Petrenko, V. F., and Whitworth, R. W. (1999). *Physics of Ice*. Oxford: Oxford University Press.

Petrov, V. A., et al. (1989). The heat capacity of liquid ethanol, as the NIST Chemistry WebBook lists it.

Pickard, G. W. (1906). “Means for receiving intelligence communicated by electric waves”. United States Patent 836,531.

Planck, M. (1901). “Ueber das Gesetz der Energieverteilung im Normalspectrum”. *Annalen der Physik* 309, 553–563.

Polanyi, M. (1934). “Über eine Art Gitterstörung, die einen Kristall plastisch machen könnte”. *Zeitschrift für Physik* 89, 660.

Pomeranchuk, I. (1950). *Zhurnal Eksperimental'noi i Teoreticheskoi Fiziki* 20, 919.

Popescu, S., Short, A. J., and Winter, A. (2006). “Entanglement and the foundations of statistical mechanics”. *Nature Physics* 2, 754–758.

Pound, R. V., and Rebka, G. A. (1960). “Apparent Weight of Photons”. *Physical Review Letters* 4, 337.

Pound, R. V., and Snider, J. L. (1964). “Effect of Gravity on Nuclear Resonance”. *Physical Review Letters* 13, 539.

Protein Data Bank. Holdings statistics, as reported for 21 May 2026. www.rcsb.org.

Prša, A., et al. (2016). “Nominal Values for Selected Solar and Planetary Quantities: IAU 2015 Resolution B3”. *Astronomical Journal* 152, 41.

Puchalski, M., Komasa, J., and Pachucki, K. (2020). “Hyperfine Structure of the First Rotational Level in H_2, D_2 and HD Molecules and the Deuteron Quadrupole Moment”. *Physical Review Letters* 125, 253001.

Purcell, E. M., Torrey, H. C., and Pound, R. V. (1946). “Resonance Absorption by Nuclear Magnetic Moments in a Solid”. *Physical Review* 69, 37.

Pusey, P. N., Zaccarelli, E., Valeriani, C., Sanz, E., Poon, W. C. K., and Cates, M. E. (2009). “Hard spheres: crystallization and glass formation”. arXiv:0908.1663.

Radzicka, A., and Wolfenden, R. (1995). “A proficient enzyme”. *Science* 267, 90–93.

Raman, C. V., and Krishnan, K. S. (1928). "A New Type of Secondary Radiation". *Nature* 121, 501.

Ramsey, N. F. (1950). "Magnetic Shielding of Nuclei in Molecules". *Physical Review* 78, 699.

Rayleigh, Lord (Strutt, J. W.) (1871). "On the light from the sky, its polarization and colour". *Philosophical Magazine* 41, 107 and 274.

Reinitzer, F. (1888). "Beiträge zur Kenntniss des Cholesterins". *Monatshefte für Chemie* 9, 421.

Reynolds, C. A., Serin, B., Wright, W. H., and Nesbitt, L. B. (1950). "Superconductivity of Isotopes of Mercury". *Physical Review* 78, 487.

Rhim, W.-K., Pines, A., and Waugh, J. S. (1971). "Time-Reversal Experiments in Dipolar-Coupled Spin Systems". *Physical Review B* 3, 684.

Rocher-Casterline, B. E., Ch'ng, L. C., Mollner, A. K., and Reisler, H. (2011). "Communication: Determination of the bond dissociation energy (D_0) of the water dimer, $(H_2O)_2$, by velocity map imaging". *Journal of Chemical Physics* 134, 211101.

Sagawa, M., Fujimura, S., Togawa, N., Yamamoto, H., and Matsuura, Y. (1984). "New material for permanent magnets on a base of Nd and Fe". *Journal of Applied Physics* 55, 2083.

Saha, M. N. (1920). "Ionisation in the solar chromosphere". *Philosophical Magazine* 40, 472.

Saminadayar, L., Glattli, D. C., Jin, Y., and Etienne, B. (1997). "Observation of the e/3 Fractionally Charged Laughlin Quasiparticle". *Physical Review Letters* 79, 2526.

Schadt, M., and Helfrich, W. (1971). "Voltage-dependent optical activity of a twisted nematic liquid crystal". *Applied Physics Letters* 18, 127.

Schmidt, T. (1937). "Über die magnetischen Momente der Atomkerne". *Zeitschrift für Physik* 106, 358–361.

Schoenflies, A. (1891). *Krystallsysteme und Krystallstructur*. Leipzig: Teubner.

Schreiner, P. R., Reisenauer, H. P., Pickard, F. C., Simmonett, A. C., Allen, W. D., Mátyus, E., and Császár, A. G. (2008). "Capture of hydroxymethylene and its fast disappearance through tunnelling". *Nature* 453, 906–909.

Sellmeier, W. (1872). "Ueber die durch die Aetherschwingungen erregten Mitschwingungen der Körpertheilchen und deren Rückwirkung auf die ersteren". *Annalen der Physik* 223, 386.

Seward, T. P., and Vascott, T., eds. (2005). *High Temperature Glass Melt Property Database for Process Modeling*. Westerville, Ohio: The American Ceramic Society.

Shannon, R. D. (1976). "Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides". *Acta Crystallographica A* 32, 751–767.

Shapiro, S. (1963). "Josephson Currents in Superconducting Tunneling: The Effect of Microwaves and Other Observations". *Physical Review Letters* 11, 80.

Shechtman, D., Blech, I., Gratias, D., and Cahn, J. W. (1984). "Metallic Phase with Long-Range Orientational Order and No Translational Symmetry". *Physical Review Letters* 53, 1951.

Shockley, W. (1949). "The theory of p-n junctions in semiconductors and p-n junction transistors". *Bell System Technical Journal* 28, 435.

Shockley, W., and Queisser, H. J. (1961). "Detailed Balance Limit of Efficiency of p-n Junction Solar Cells". *Journal of Applied Physics* 32, 510–519.

Shull, C. G., and Smart, J. S. (1949). "Detection of Antiferromagnetism by Neutron Diffraction". *Physical Review* 76, 1256.

Smit, J., and Wijn, H. P. J. (1959). *Ferrites*. Eindhoven: Philips Technical Library.

Sommerfeld, A. (1914). "Über die Fortpflanzung des Lichtes in dispergierenden Medien". *Annalen der Physik* 44, 177.

Sommerfeld, A. (1928). "Zur Elektronentheorie der Metalle auf Grund der Fermischen Statistik". *Zeitschrift für Physik* 47, 1.

Souris, F., Grucker, J., Dupont-Roc, J., and Jacquier, Ph. (2010). "Investigating metastable hcp solid helium below its melting pressure". arXiv:1011.2297.

Span, R., and Wagner, W. (1996). "A New Equation of State for Carbon Dioxide Covering the Fluid Region from the Triple-Point Temperature to 1100 K at Pressures up to 800 MPa". *Journal of Physical and Chemical Reference Data* 25, 1509.

Sproul, A. B., and Green, M. A. (1991). "Improved value for the silicon intrinsic carrier concentration from 275 to 375 K". *Journal of Applied Physics* 70, 846–854.

Srednicki, M. (1994). "Chaos and quantum thermalization". *Physical Review E* 50, 888.

Stefan, J. (1879). "Über die Beziehung zwischen der Wärmestrahlung und der Temperatur". *Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften, Mathematisch-Naturwissenschaftliche Classe* 79, 391–428.

Stoner, E. C. (1938). "Collective electron ferromagnetism". *Proceedings of the Royal Society of London A* 165, 372.

Stritzker, B., and Buckel, W. (1972). "Superconductivity in the palladium-hydrogen and the palladium-deuterium systems". *Zeitschrift für Physik* 257, 1.

Suen, Y. W., Engel, L. W., Santos, M. B., Shayegan, M., and Tsui, D. C. (1992). "Observation of a $\nu = 1/2$ fractional quantum Hall state in a double-layer electron system". *Physical Review Letters* 68, 1379.

Sze, S. M., and Ng, K. K. (2007). *Physics of Semiconductor Devices*. 3rd edition. Hoboken, New Jersey: Wiley.

Szilard, L. (1929). "Über die Entropieverminderung in einem thermodynamischen System bei Eingriffen intelligenter Wesen". *Zeitschrift für Physik* 53, 840–856.

Taylor, G. I. (1934). "The Mechanism of Plastic Deformation of Crystals. Part I. Theoretical". *Proceedings of the Royal Society of London A* 145, 362.

Thompson, A. C., et al. (2009). *X-Ray Data Booklet*. Berkeley, California: Lawrence Berkeley National Laboratory.

Thomson, J. J. (1897). "Cathode Rays". *Philosophical Magazine*, Series 5, 44, 293–316.

Thouless, D. J., Kohmoto, M., Nightingale, M. P., and den Nijs, M. (1982). "Quantized Hall Conductance in a Two-Dimensional Periodic Potential". *Physical Review Letters* 49, 405.

Tisza, L. (1938). "Transport Phenomena in Helium II". *Nature* 141, 913.

Tolman, R. C., Ehrenfest, P., and Podolsky, B. (1931). "On the Gravitational Field Produced by Light". *Physical Review* 37, 602.

Tonomura, A., Osakabe, N., Matsuda, T., Kawasaki, T., Endo, J., Yano, S., and Yamada, H. (1986). "Evidence for Aharonov-Bohm effect with magnetic field completely shielded from electron wave". *Physical Review Letters* 56, 792.

Tropf, W. J., Harris, T. J., and Thomas, M. E. (2000). "Optical materials: visible and infrared". In *Electro-Optics Handbook*, 2nd edition. New York: McGraw-Hill.

Tsai, J.-S., Jain, A. K., and Lukens, J. E. (1983). "High-Precision Test of the Universality of the Josephson Voltage-Frequency Relation". *Physical Review Letters* 51, 316.

Tsui, D. C., Störmer, H. L., and Gossard, A. C. (1982). "Two-Dimensional Magnetotransport in the Extreme Quantum Limit". *Physical Review Letters* 48, 1559.

U.S. Department of Energy, Solar Decathlon. "Technology Spotlight: Heat Pumps". www.solardecathlon.gov.

Urey, H. C., Brickwedde, F. G., and Murphy, G. M. (1932). "A Hydrogen Isotope of Mass 2". *Physical Review* 39, 164–165.

van der Waals, J. D. (1873). *Over de Continuïteit van den Gas- en Vloeistoftoestand*. Doctoral thesis, Leiden.

Vinen, W. F. (1961). "The detection of single quanta of circulation in liquid helium II". *Proceedings of the Royal Society of London A* 260, 218–236.

Volz, U., Majerus, M., Liebel, H., Schmitt, A., and Schmoranzer, H. (1996). "Precision Lifetime Measurements on NaI 3p $^2P_{1/2}$ and 3p $^2P_{3/2}$ by Beam-Gas-Laser Spectroscopy". *Physical Review Letters* 76, 2862–2865.

von Klitzing, K., Dorda, G., and Pepper, M. (1980). "New Method for High-Accuracy Determination of the Fine-Structure Constant Based on Quantized Hall Resistance". *Physical Review Letters* 45, 494.

Wagner, W., and Pruß, A. (2002). "The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use". *Journal of Physical and Chemical Reference Data* 31, 387–535.

Watson, J. D., and Crick, F. H. C. (1953). "Molecular Structure of Nucleic Acids: A Structure for Deoxyribose Nucleic Acid". *Nature* 171, 737–738.

Wei, L., Kuo, P. K., Thomas, R. L., Anthony, T. R., and Banholzer, W. F. (1993). "Thermal conductivity of isotopically modified single crystal diamond". *Physical Review Letters* 70, 3764.

Weiss, P. (1907). "L'hypothèse du champ moléculaire et la propriété ferromagnétique". *Journal de Physique Théorique et Appliquée* 6, 661.

Westheimer, F. H. (1961). "The Magnitude of the Primary Kinetic Isotope Effect for Compounds of Hydrogen and Deuterium". *Chemical Reviews* 61, 265.

Weyl, H. (1929). "Elektron und Gravitation. I". *Zeitschrift für Physik* 56, 330–352.

Wigner, E. (1939). "On Unitary Representations of the Inhomogeneous Lorentz Group". *Annals of Mathematics* 40, 149–204.

Willett, R., Eisenstein, J. P., Störmer, H. L., Tsui, D. C., Gossard, A. C., and English, J. H. (1987). "Observation of an even-denominator quantum number in the fractional quantum Hall effect". *Physical Review Letters* 59, 1776.

Wilson, A. H. (1931). "The theory of electronic semi-conductors". *Proceedings of the Royal Society of London A* 133, 458.

Wood, R. W. (1933). "Remarkable Optical Properties of the Alkali Metals". *Physical Review* 44, 353.

Wood, W. W., and Jacobson, J. D. (1957). "Preliminary Results from a Recalculation of the Monte Carlo Equation of State of Hard Spheres". *Journal of Chemical Physics* 27, 1207.

Xia, Y., et al. (2009). "Observation of a large-gap topological-insulator class with a single Dirac cone on the surface". *Nature Physics* 5, 398.

Yang, C. N., and Mills, R. L. (1954). "Conservation of Isotopic Spin and Isotopic Gauge Invariance". *Physical Review* 96, 191.

Yarmchuk, E. J., Gordon, M. J. V., and Packard, R. E. (1979). "Observation of Stationary Vortex Arrays in Rotating Superfluid Helium". *Physical Review Letters* 43, 214.

Yarnell, J. L., Katz, M. J., Wenzel, R. G., and Koenig, S. H. (1973). "Structure Factor and Radial Distribution Function for Liquid Argon at 85 K". *Physical Review A* 7, 2130.

Yukawa, H. (1935). "On the Interaction of Elementary Particles. I". *Proceedings of the Physico-Mathematical Society of Japan* 17, 48–57.

Zanotto, E. D. (1998). "Do cathedral glasses flow?". *American Journal of Physics* 66, 392–395.

Zhang, H., Liu, C.-X., Qi, X.-L., Dai, X., Fang, Z., and Zhang, S.-C. (2009). "Topological insulators in Bi_2Se_3, Bi_2Te_3 and Sb_2Te_3 with a single Dirac cone on the surface". *Nature Physics* 5, 438.

Zurek, W. H. (2003). "Decoherence, einselection, and the quantum origins of the classical". *Reviews of Modern Physics* 75, 715.

Zwanenburg, F. A., Dzurak, A. S., Morello, A., Simmons, M. Y., Hollenberg, L. C. L., Klimeck, G., Rogge, S., Coppersmith, S. N., and Eriksson, M. A. (2013). "Silicon quantum electronics". *Reviews of Modern Physics* 85, 961.

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