

## Seven Steps to Quantum Physics

The first quarter of the twentieth century was a period of transition for theoretical physics. Classical physics had broken down, but there was as yet no coherent theory to replace it, only disconnected fragments. Gradually, in the minds of a few people, these fragments began to fit together into a new and strange shape. We can best understand the novel features of the picture that finally emerged by retracing the path that led to it—not the actual historical path, with all its twists, turns, branchings, and detours, but the shorter and simpler path that emerges when we look at the past through the eyes of the present. Historians rightly disparage this way of viewing the past (“Whig history”), but our concern here is not so much with history as with genealogy—the genealogy of ideas.

### Step 1: Boltzmann's Theory of Entropy

The story as it is usually told begins in 1900 with Max Planck's theory of black-body radiation. It should begin almost thirty years earlier with Ludwig Boltzmann's theory of entropy. I described that theory in Chapter 2, but in so doing I glossed over an important difficulty. Boltzmann's solution to this difficulty set Planck on the path that eventually led to quantum physics.

Boltzmann identified the entropy of a physical system in a given macrostate with the randomness of that macrostate. He defined the randomness of a macrostate as the logarithm of the number of its microstates. Let's try to apply this definition to a gas. In Chapter 3 we represented the state of a single molecule by a point in a six-dimensional space. Three of the point's six coordinates specify



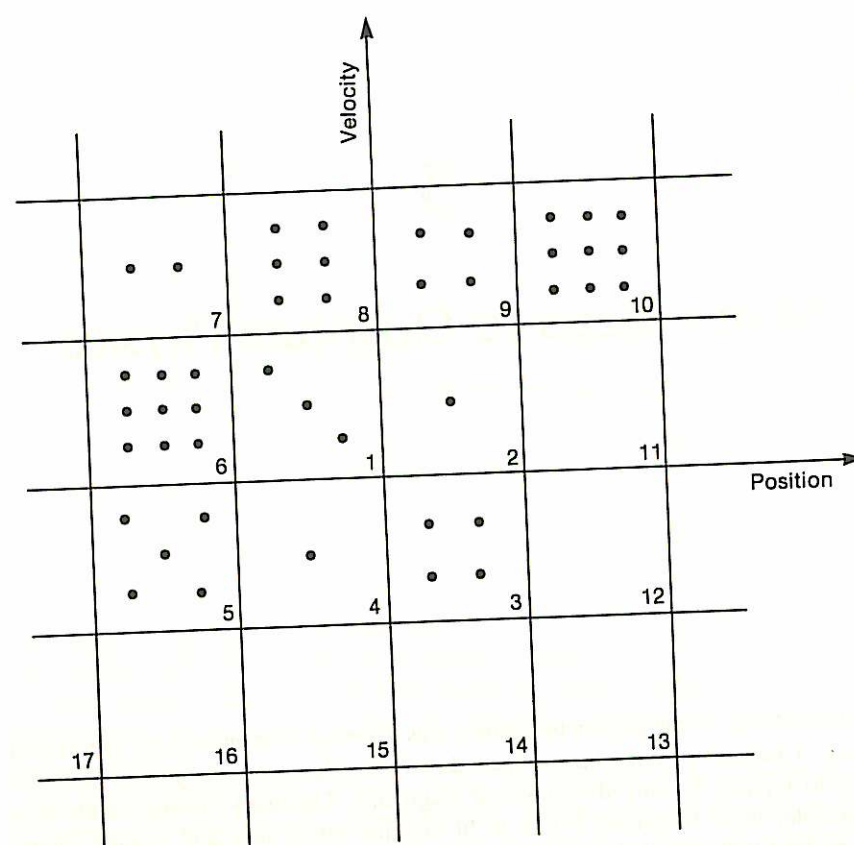


FIGURE 5.1 Numbered macrocells in the two-dimensional state space of a particle moving along a line. Each macrocell represents a range of possible positions and velocities. To specify the macrostate of a gas consisting of such particles, we have to specify the number of particles in each macrocell. There are three particles in cell 1, one in cell 2, four in cell 3. The macrostate of the gas is specified by a series of numbers that begins 3, 1, 4, 1, 5, 9, 2, 6, 4, 9.

the molecule's position; the other three specify its velocity. To describe the state of a pair of molecules, we used a twelve-dimensional space. But we could equally well have represented the state of a pair of particles by a pair of points in a common six-dimensional position-velocity space. For our present purpose the second representation is more convenient. We represent the *microstate* of a gas consisting of  $N$  molecules by a set of  $N$  points in the six-dimensional space.

To define the *macrostates* of a single molecule, we divide the six-dimensional space into equal compartments, which I will call *macrocells* (Figure 5.1). Every macrocell represents a possible macrostate of a single molecule. The points in a macrocell represent the microstates that make up the macrostate. When we say that a molecule is in a certain macrostate, we mean that its position and velocity lie within the limits that define the corresponding macrocell.

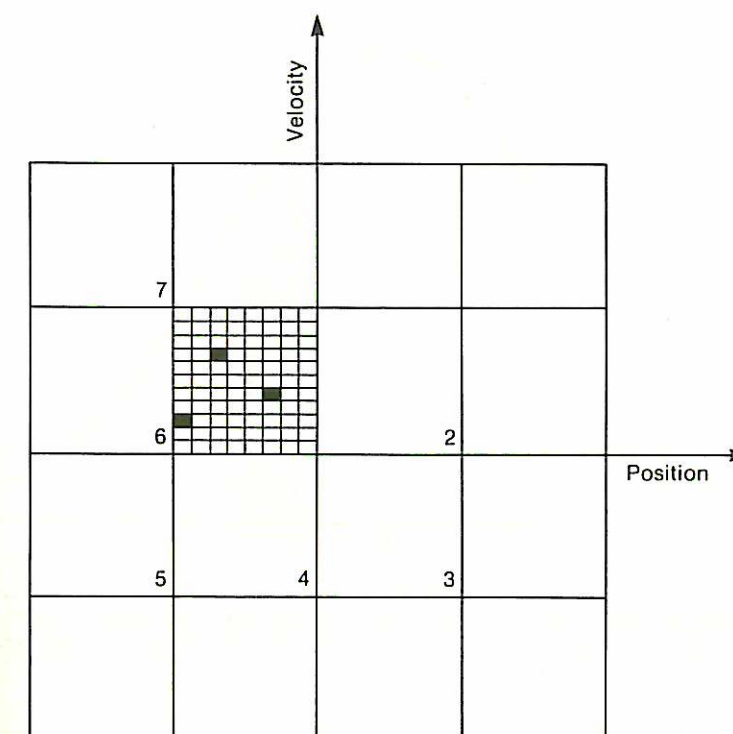


FIGURE 5.2 Each macrocell is divided into a large number of equal microcells small enough to ensure that none contains more than one particle.

The macrostate of a *gas* is defined by the way in which the points that represent molecular microstates are distributed among the macrocells. To specify a macrostate of the gas, we have to specify how many representative points (points representing the microstates of individual molecules) lie in each macrocell.

So far, so good. Now let's try to calculate the randomness of a macrostate. The first step is to count the microstates belonging to that macrostate. Consider, for simplicity, a gas consisting of a single molecule. We specify its macrostate by pointing to a particular macrocell. The points belonging to that macrocell represent its microstates. But the number of points in any macrocell is infinite, so the calculation breaks down. (Actually, the difficulty is even more severe. The set of points in a macrocell is not only infinite, but also *uncountable*. See Chapter 1, note 9.)

Boltzmann got around this difficulty by assuming that a molecule's possible microstates are represented not by points in the six-dimensional position-velocity space but by identical, very small cells (*microcells*), as in Figure 5.2. He stipulated that these cells should be so small that they almost never contain more than one representative point. It is then relatively easy to figure out how many microstates belong to any given macrostate, and thus to calculate the randomness of that macrostate.



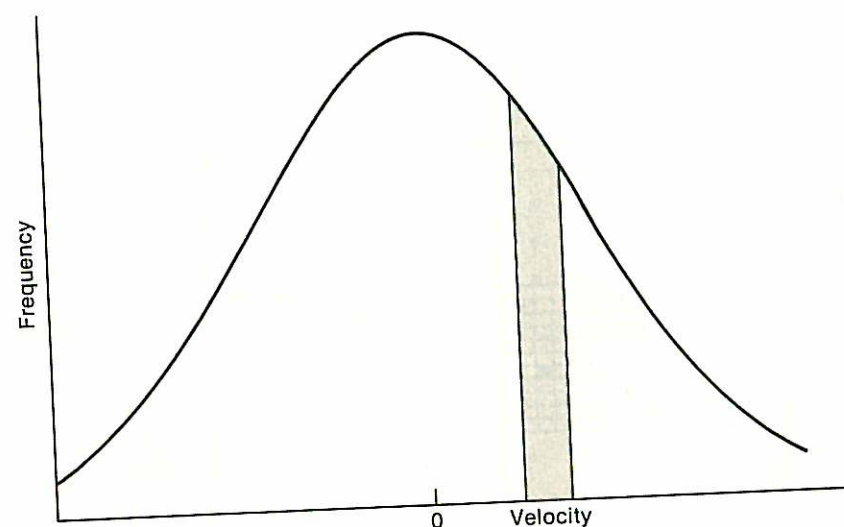


FIGURE 5.3 Statistical profile of velocities in any given direction. If the total area under the curve is unity, the area of a vertical slice like that indicated in the figure is equal to the fraction of the molecules that have velocity components within the limits that define the slice.

But doesn't the result of the calculation depend on the size of the microcells? Yes, but in what proves to be a "harmless" way. Changing the size of the microcells causes the number of microstates in any given macrostate to be multiplied by a certain number—the same number for every macrostate. Because the randomness of a macrostate is the logarithm of the number of its microstates and the logarithm converts products into sums, changing the size of the microcells increases the randomness of every macrostate by the same amount. Thus the *difference* between the randomnesses of any two macrostates doesn't change. In nearly all scientific applications, we are interested in how the randomness (or entropy) of a system changes, not in its absolute value. For example, chemical reactions in a living cell generate entropy and thereby decrease the cell's store of potentially useful energy. The entropy generated is the difference between the entropies of the final and the initial states, so we can calculate it without specifying the size of the microcells.

Let's take a closer look at Boltzmann's way of calculating the randomness of a gas. Its molecules are moving in all directions with a wide range of speeds. Boltzmann's aim was to predict the *statistical profile* of molecular velocities in a given direction (Figure 5.3). Assume that the gas is in a box whose walls are kept at a fixed temperature. This temperature determines the average kinetic energy of the gas molecules and hence their average squared velocity. (The kinetic energy of a particle is proportional to the square of its velocity.) Stipulating that the temperature of the gas has a given value therefore imposes a constraint on the statistical profile of molecular velocities: the profile must have a shape that gives

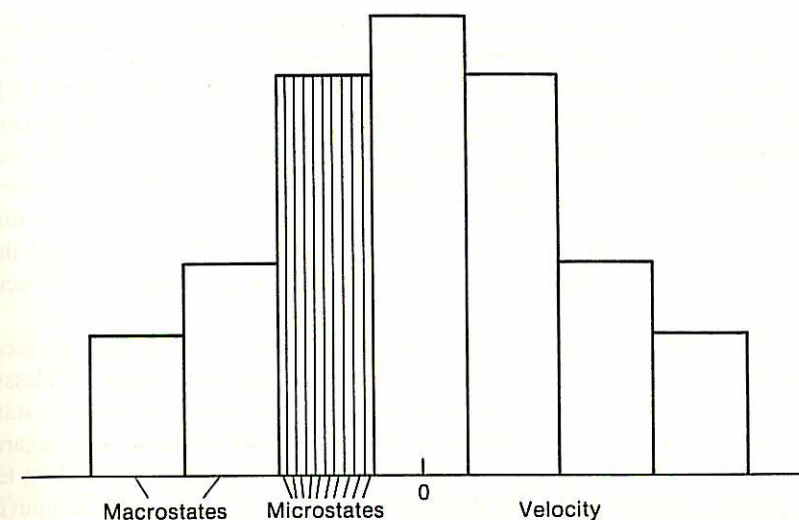


FIGURE 5.4 Discrete representation of the statistical profile of velocities of gas molecules in a given direction. The large velocity intervals, greatly exaggerated in this diagram, represent velocity macrostates. The small intervals, whose size is even more greatly exaggerated, represent velocity microstates.

the average squared velocity the value appropriate to that temperature. Physically, this constraint means that there is a fixed quantity of energy to be distributed among the molecules. The combined kinetic energy of the molecules is proportional to both the absolute temperature and the number of molecules. A vast number of velocity profiles satisfy this constraint. Which is the right profile?

We may approximate the statistical profile of molecular velocities in a given direction by a bar graph (Figure 5.4). The velocity intervals in this graph represent velocity macrocells, and the graph itself defines a possible *macrostate* of the gas. (Distinct macrostates have distinct graphs.) Next we divide each velocity interval into smaller intervals, as illustrated in Figure 5.4. These represent velocity microcells. Every way of distributing the molecules among microcells represents a possible *microstate* of the gas. Every microstate belongs to a definite macrostate, because every way of distributing the molecules among microcells defines a way of distributing the molecules among macrocells.

A gas molecule undergoes a huge number of collisions every second. Because molecular collisions cause random changes in the molecular velocities, it seems plausible that the macrostate of a gas that has been left to itself for a long time should be as random as it can be, subject to the constraint that the combined kinetic energy of the molecules has a fixed value. Now according to Boltzmann's definition, the randomness of a macrostate is equal to the logarithm of the number of its microstates. Hence the most random macrostate is the one with the greatest number of microstates. The velocity profile that satisfies this condition isn't difficult to calculate. It is the bell-shaped curve illustrated in Figure 5.3.

Boltzmann's theory was spectacularly successful. By reproducing all the old



laws of thermodynamics, it demonstrated that thermodynamics is at bottom a statistical theory of molecules moving and interacting according to the laws of Newtonian physics. Thus it provided the last span in a bridge that Maxwell and Clausius had begun to build some years earlier between the island of thermodynamics and the mainland of classical mechanics. But Boltzmann's theory did even more. It described a wide range of important phenomena that lie outside the domain of classical thermodynamics, such phenomena as heat conduction, molecular diffusion, and the viscous decay of internal motions in a gas. The rates of all these processes could now be deduced from the properties of molecules and molecular interactions.

Yet Boltzmann's theory seemed to be built on sand, for his use of microcells to calculate the entropy blatantly contradicted a fundamental tenet of classical physics: that a freely moving particle has a continuous range of possible states, represented not by cells but by points. Boltzmann himself seems to have regarded the use of microcells as a harmless computational device, and many modern textbooks present it in that way. But microcells aren't really a computational device. Instead of facilitating a difficult calculation, as computational devices are supposed to do, they allowed Boltzmann to replace a legitimate calculation that gave a meaningless answer with an illegitimate calculation that gave what was demonstrably the right answer.

Had Boltzmann been gifted with second sight and an unnatural degree of self-confidence, he might have argued as follows: "My theory of entropy rests on a premise that contradicts a basic tenet of classical physics. My theory is clearly right. Therefore its premise must be right. So classical physics must be wrong." As we will see, an argument of this kind was actually made by Albert Einstein thirty years later in a closely related context. But Boltzmann's "computational device" wasn't legitimized until 1925—more than half a century after he first used it. Quantum physics represents the microstates of a particle by cells of finite and fixed volume in six-dimensional position-velocity space.

## Step 2: Planck's Theory of Blackbody Radiation

An evacuated box whose walls are kept at a fixed temperature contains an intangible "gas"—light emitted by the heated walls. Like an ordinary gas, light carries energy and exerts pressure, both of which increase with the temperature of the walls. Experiments show that the light, like the gas, eventually settles into a state of equilibrium in which all its measurable properties are determined by the temperature of the walls. Light in this state is called *blackbody radiation*.

In the late nineteenth century, physicists began to study the *spectrum* of blackbody radiation and its dependence on temperature. (By the spectrum of blackbody radiation, I mean the curve that specifies how the intensity of the radiation varies with color or wavelength.) Theorists made some progress. They showed that if the spectrum is known for a single temperature, it can then be calculated for any other temperature by means of a simple rule. But in spite of strenuous efforts, they failed to predict the spectrum. Meanwhile, experimenters were trying to mea-

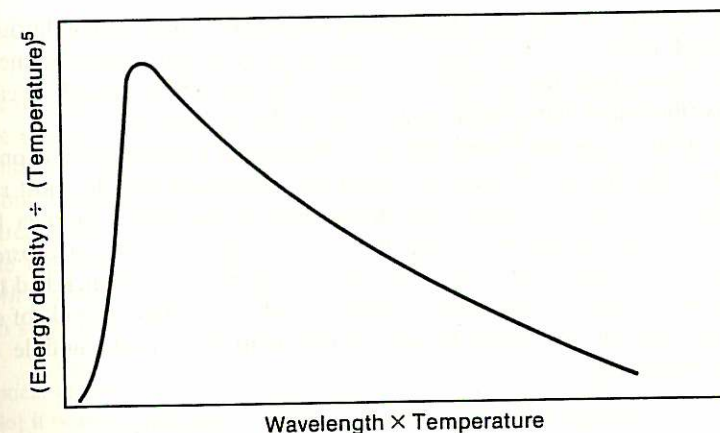


FIGURE 5.5 Spectral distribution of blackbody radiation. "Energy density" means energy per unit volume and per unit wavelength; "temperature" means absolute temperature. If energy density divided by the fifth power of the temperature is plotted against the product of wavelength and temperature, a single curve represents the spectral distribution of radiant energy at any given temperature. Thus the wavelength at which the curve peaks is inversely proportional to the absolute temperature, and the area under the curve, which represents the radiant energy per unit volume, is proportional to the fourth power of the absolute temperature.

sure it. Early in the year 1900 they succeeded, obtaining the curve shown in Figure 5.5

Max Planck had been grappling with this theoretical problem for several years. He had also been keeping a close watch on the experiments. As soon as he heard about the new measurements, he began to look for a formula that would fit them and that would also satisfy the known theoretical constraints. He soon found one. But even knowing what he was convinced was the correct formula, he couldn't derive it theoretically. At this point Planck turned to Boltzmann's theory of randomness, to which he had previously paid little attention. He set out to adapt Boltzmann's way of calculating the most random distribution of molecular velocities to the problem of predicting the most random spectral distribution of light.

Planck considered a box filled with light and with a gas composed of rather peculiar molecules. Each molecule consisted of an electron vibrating inside an extended spherical cloud of positive electric charge. According to Maxwell's electromagnetic theory, such a system absorbs and emits light of a single wavelength. The *frequency* (reciprocal period) of the absorbed or emitted light waves is equal to the vibrating electron's frequency of vibration. Planck reasoned that in the most random state, the combined energy of the light and the gas would be split three ways. Part of the energy would be in the form of light; part of it would be in the form of kinetic energy associated with the motions of whole molecules; and part of it would be in the form of energy associated with the vibrations of electrons within individual molecules. The third share, vibrational energy, was the crucial one. If he could calculate how it was distributed among the molecules, he would



be able to deduce the spectrum of the light; for he knew that, in equilibrium, the rates at which molecules absorb and emit energy must be equal, and he knew how to calculate those rates for a vibrating electron. So everything hinged on calculating the distribution of vibrational energy among the molecules.

It was at this point that Planck turned to Boltzmann's earlier calculation of the most random distribution of molecular velocities. He found that the most random distribution of vibrational energy did indeed lead to his earlier formula for the spectrum of blackbody radiation, but only if he assumed that *the microstates of vibrational energy form a discrete aggregate*. More precisely, Planck had to postulate that the energy of a vibrating electron is made up of finite parcels of energy and that the size of an energy parcel (or quantum) is a fixed multiple of the vibrational frequency:

$$\text{energy quantum} = \text{fixed constant} \times \text{frequency}$$

Physicists call the fixed constant Planck's constant and represent it by the letter  $h$ .

In replacing the classical continuum of vibrational energies by a discrete aggregate, Planck was following in Boltzmann's footsteps. But in Boltzmann's calculation of the most random velocity distribution, the exact size of the microcells didn't matter. In Planck's derivation, the size of the energy packets—that is, the value of the constant  $h$ —was crucial. To make the predicted blackbody curve agree with experiment, Planck had to set the constant  $h$  equal to a specific number, whose value could be deduced from the curve's measured shape.

Planck himself found this very puzzling, as he tells us in reminiscences published forty-three years later:

Now the theoretically most difficult problem arose of giving a physical meaning to this peculiar constant [ $h$ ], whose introduction meant a break with classical theory that was much more fundamental than I had suspected at the outset. . . . Over a period of many years I tried again and again to fit [it] into the framework of classical physics.<sup>1</sup>

### Step 3: The Discreteness of Light

Einstein, who was twenty-two years old when Planck's paper appeared, became convinced that Planck's constant and the discreteness that it symbolized would never fit into the framework of theoretical physics. In a paper entitled "On a Heuristic Point of View about the Creation and Conversion of Light," published in 1905, he put forward the bold hypothesis that monochromatic light of frequency  $f$  can be emitted or absorbed only in discrete packets, or quanta, of energy  $hf$ . (Monochromatic light is light of a single color or frequency. Newton discovered that a prism separates light into monochromatic rays, which can't be further split up. Monochromatic rays—or rather, their energy quanta—are thus the elementary constituents of light, in somewhat the same way that molecules are the elementary constituents of a gas.)

Einstein's hypothesis flouted conventional wisdom. Planck and nearly every-

one else believed, and continued to believe for many years after the publication of Einstein's paper, that classical electromagnetic theory fully and correctly describes light itself, if not the interaction between light and matter. They assumed that the origin of the mysterious discreteness that Planck had been forced to introduce into his derivation lay elsewhere. Characteristically, Einstein met this plausible (but unfounded) belief head-on. His paper opens with the remark that physicists treat matter and light differently: they assume that matter is fundamentally discrete but that light is fundamentally continuous. Perhaps, he suggested, they are *both* discrete. True, the wave theory of light works very well and is probably here to stay, but

optical observations refer to time averages and not to instantaneous values. . . . [So] it is quite conceivable that [the wave theory] will lead to contradictions when it is applied to the phenomena of the creation and conversion of light.<sup>2</sup>

What Einstein had in mind was that a beam of light might be made up of *spatially* distinct units, like a beam of particles. But this was just a picture accompanying his actual hypothesis: that monochromatic light of frequency  $f$  can gain or lose energy to matter only in packets of magnitude  $hf$ .

To justify this hypothesis, Einstein showed that the entropy of monochromatic light of sufficiently high frequency is given by a formula that coincides with Boltzmann's formula for the entropy of an ordinary gas if, in that formula, the number of particles is set equal to the energy of the light divided by Planck's energy quantum. In other words, the entropy of high-frequency light is the same as the entropy of gas whose molecules are Planck's energy quanta.

Einstein proposed three experimental tests of this hypothesis.

1. *Photoluminescence.* A photoluminescent substance absorbs light of one frequency and emits light of another frequency. Einstein's hypothesis predicts that the frequency of the emitted light should always be less than that of the absorbed light. For example, a photoluminescent substance could absorb ultraviolet light and emit yellow light but it couldn't, according to Einstein's hypothesis, absorb yellow light and emit violet light. Why? When I buy something with a dollar bill, the change is always less than a dollar. A photoluminescent substance that has absorbed a quantum of energy emits a quantum of smaller energy and hence lower frequency. The rest of the energy may be emitted at another frequency, as illustrated in Figure 5.6.

2. *Photoionization.* Physicists had noticed that an electrically nonconducting gas may become conducting after it has been irradiated with ultraviolet light, but not with visible or infrared light. According to Einstein's hypothesis, ultraviolet light consists of more energetic quanta than visible light. An ultraviolet quantum may transfer enough energy to an electron bound in a gas molecule to tear the electron loose (Figure 5.7). Unbound electrons (and positively charged ions) can move freely through a gas in response to an applied electric field, so an ionized gas conducts electricity.

3. *The photoelectric effect.* Light falling on the surface of some metals causes



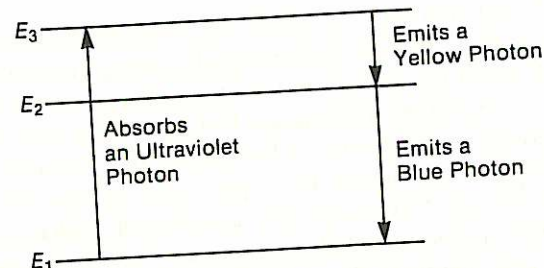


FIGURE 5.6 Photoluminescence. The molecules of a photoluminescent substance are normally in their state of lowest energy  $E_1$ . If a molecule is in the excited state of energy  $E_3$ , it can emit a visible photon by jumping to an intermediate state whose energy  $E_2$  lies between  $E_1$  and  $E_3$ . A second jump, back to the ground state, may also be accompanied by the emission of a visible photon. To get to state  $E_3$ , however, the molecule must absorb an ultraviolet photon whose energy is at least as great as the energy difference between  $E_3$  and  $E_1$  divided by Planck's constant.

electrons to be ejected. Einstein's explanation of this phenomenon is similar to his explanation of photoionization. An electron bound in a metallic lattice (which we may think of as a large molecule with repetitive structure) may acquire enough energy to break free from the lattice if the lattice absorbs a sufficiently energetic light quantum. Just as is true for photoionization, the quality (that is, color) of the light is what counts. Weak ultraviolet light falling on a photosensitive metal causes electrons to be ejected, albeit slowly; red light, however intense, is completely ineffective.

All three predictions were consistent with the experimental data then available, but the experiments were not good enough to provide a crucial test. In both photoionization and the photoelectric effect, part of the absorbed quantum of energy is used to liberate an electron from an atom, a molecule, or a crystal lattice. The rest of the energy appears as the kinetic energy of the ejected electron. Thus electrons ejected by light of relatively high frequency should be moving faster than electrons ejected by light of lower frequency. Robert A. Millikan, who first accurately measured the electric charge of a single electron, set out to test this prediction for the photoelectric effect. In 1915, he summarized his results, and his conclusions about Einstein's hypothesis, in these words:

Einstein's photoelectric equation . . . appears in every case to predict exactly the observed results. . . . Yet the semicorpuscular theory by which Einstein arrived at his equation seems at present wholly untenable.<sup>3</sup>

Not just untenable, but "wholly untenable." Abraham Pais has remarked that Millikan's attitude toward the hypothesis that light exchanges energy with matter only in discrete packets was not unrepresentative: "Rather, the physics community at large had received . . . the hypothesis with disbelief and with skepticism bordering on derision."<sup>4</sup>

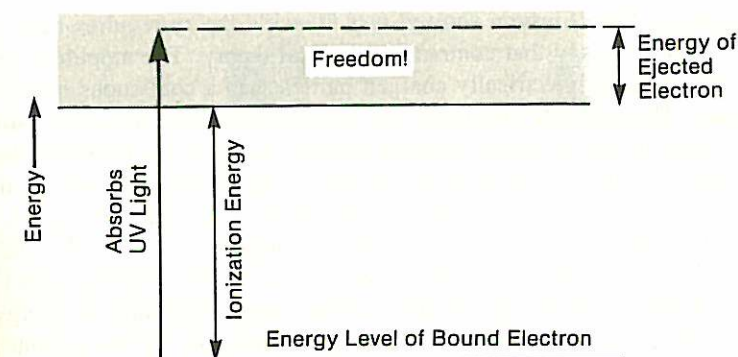


FIGURE 5.7 Photoionization. An ultraviolet quantum may transfer enough energy to an electron bound in a gas molecule to tear the electron loose. An ionizing photon's frequency must exceed the ionization energy divided by Planck's constant.

The 1905 paper has another interesting feature. Einstein visualized energy quanta as localized in space:

*According to the assumption considered here, when a light ray starting from a point is propagated, the energy is not continuously distributed over an ever-increasing volume but consists of a finite number of energy quanta, localized in space, which move without being divided and which can be absorbed or emitted only as a whole.* (italics added)

This sentence summarizes Einstein's conclusion. But what his argument actually establishes—or at least makes highly plausible—is conveyed by the part of the sentence that I've italicized:

[The energy carried by a light ray] consists of a finite number of energy quanta which can be absorbed or emitted only as a whole.

The nonitalicized parts of the original sentence convey a *picture* of energy quanta: they are localized in space and move without being divided. This may be the only picture one can form of energy quanta that is consistent with their testable properties. It doesn't follow that the picture is true, however. A modern physicist would say that energy quanta can't be pictured at all; certainly they can't be localized. Although Einstein continued to believe in the possibility of describing nature in a way that can be pictured, in his later papers on quantum physics he scrupulously refrained from drawing conclusions that went beyond the strict limits of his mathematical arguments.

#### Step 4: Energy Levels

As we saw, Planck derived his radiation formula by considering the interaction between blackbody radiation and a collection of tiny oscillators tuned to precise



frequencies. In 1906 Einstein showed that Planck's theory requires these oscillators to behave in a way that contradicts classical theory. The amplitude of vibration of an oscillating electrically charged particle has a continuous range of possible values. The larger the amplitude, the greater the vibrational energy. Moreover, classical electromagnetic theory predicts that the energy of the oscillator decreases or increases continuously as it emits or absorbs light. Einstein showed that this picture can't be valid for the oscillators that figure in Planck's theory. A Planck oscillator must have a discrete set of possible energies:  $0$ ,  $hf$ ,  $2hf$ ,  $3hf$ , and so on, where, as before,  $h$  denotes Planck's constant and  $f$  denotes the frequency of the oscillator. Furthermore, when a Planck oscillator emits or absorbs an energy quantum, its energy must decrease or increase *discontinuously* by the amount  $hf$ . Although these conclusions were logically entailed by Planck's theory, Einstein's energy-quantum hypothesis, and the principle of conservation of energy, they blatantly contradicted classical electromagnetic theory, which says that an oscillating electric charge radiates energy continuously. But the worst was yet to come.

During the first decade of the twentieth century, most physicists subscribed to a model of the atom invented by J. J. Thomson, the discoverer of electrons. Thomson's atom has pointlike electrons embedded in a sphere of positive electricity, like blueberries in a blueberry muffin. Planck's oscillators are the simplest exemplars of this model. According to classical electromagnetic theory, stable configurations of this kind do exist, and an electron vibrating about its equilibrium position does emit light of a definite frequency, so Thomson's model had much to recommend it. True, it didn't behave as Einstein said an oscillator should behave, emitting energy in discontinuous bursts, but few people took Einstein's argument seriously.

In 1911, the bubble burst. Ernest Rutherford and two assistants, Hans Geiger and E. Marsden, discovered experimentally that real atoms don't in the least resemble Thomson's model. Instead, they are constructed like miniature solar systems, with the nucleus playing the part of the Sun and the electrons the part of the planets. But if such an atom obeyed Newton's and Maxwell's laws, it couldn't possibly emit or absorb radiation at only a discrete set of frequencies; it would emit and absorb a continuous band of frequencies.

Inspired by Rutherford's discovery and Einstein's deductions about energy quanta and the quantized energy states of Planck oscillators, Niels Bohr set out to construct a new atomic theory. He began by laying down two postulates:

1. The energy of an atom or a molecule has a discrete set of possible values. Every atom and molecule has its own set of possible energies, or *energy levels*.
2. Changes in the energy of an atom or a molecule take place discontinuously, in quantum jumps. The energy gained or lost in a quantum jump may be supplied or taken by another object (for example, an electron or another atom) or by light. In the second case, a single energy quantum is absorbed or emitted.

Both rules generalize deductions that Einstein had made earlier in specific contexts (Figures 5.6 and 5.7). Their importance lay not only in this fact, but also

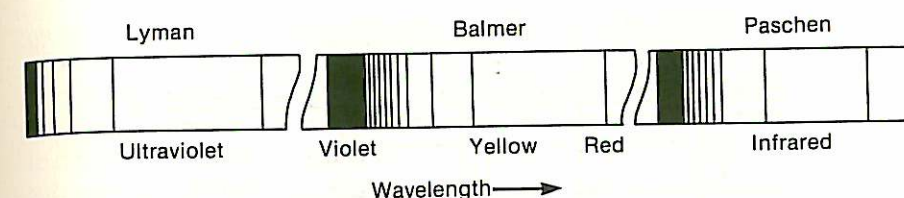


FIGURE 5.8 The spectrum of atomic hydrogen is a series of series. The first series, the Lyman series, is produced by transitions from the ground state to states of higher energy. The second series, the Balmer series, is produced by transitions from the first excited state to states of higher energy, and so on.

in the fact that they offered a new and fruitful starting point for the analysis of atomic and molecular spectra. Consider the spectrum of hydrogen (Figure 5.8). It consists of several distinct series of lines. The first series (the Lyman series) is in the ultraviolet part of the spectrum; the second (the Balmer series) is in the visible part of the spectrum; the third (the Paschen series) is in the infrared; and so on. With the help of Bohr's second rule, which connects the frequencies of spectral lines with differences between energy levels, we can construct an energy-level diagram (Figure 5.9) that represents all these series and predicts many others whose wavelengths fall outside the range accessible to laboratory spectroscopy. For example, quantum jumps between adjacent high-lying levels give rise to radio waves. Astronomers have actually observed this radio-frequency radiation, emitted by hydrogen atoms in interstellar space.

Bohr was not content with stating these rules. He set himself the task of reconciling Rutherford's planetary model of the hydrogen atom with the energy-level diagram shown in Figure 5.9. Consider, to begin with, what classical physics has to say about Rutherford's model. The force of attraction between the positively charged nucleus of a hydrogen atom and the negatively charged electron is qualitatively identical with the gravitational attraction between the Sun and a planet: both are proportional to the inverse square of the distance between the attracting bodies. Since the possible orbits of a planet are ellipses with the Sun at one focus, the possible orbits of the electron in a hydrogen atom should be ellipses with the nucleus at one focus. According to Newton's theory, the energy of a particle moving in such an orbit depends only on the size of the orbit's larger diameter and not on the ratio between the small and the large diameters. Thus infinitely many orbits correspond to a given value of the energy (those with a given major diameter and all possible values of the minor diameter), and the energy itself can have any negative value. (Positive values of the energy correspond to hyperbolic orbits.)

These predictions clash with the requirement that the hydrogen atom have a discrete set of possible states and energy levels. But Bohr, in 1913, was not willing to abandon Newton's theory outright. Einstein had shown that a Planck oscillator must have a discrete set of energy levels. Bohr asked himself: Is there an analogous rule that selects the possible orbits of an electron in a hydrogen atom from the continuously infinite set of orbits allowed by Newton's theory?<sup>5</sup>



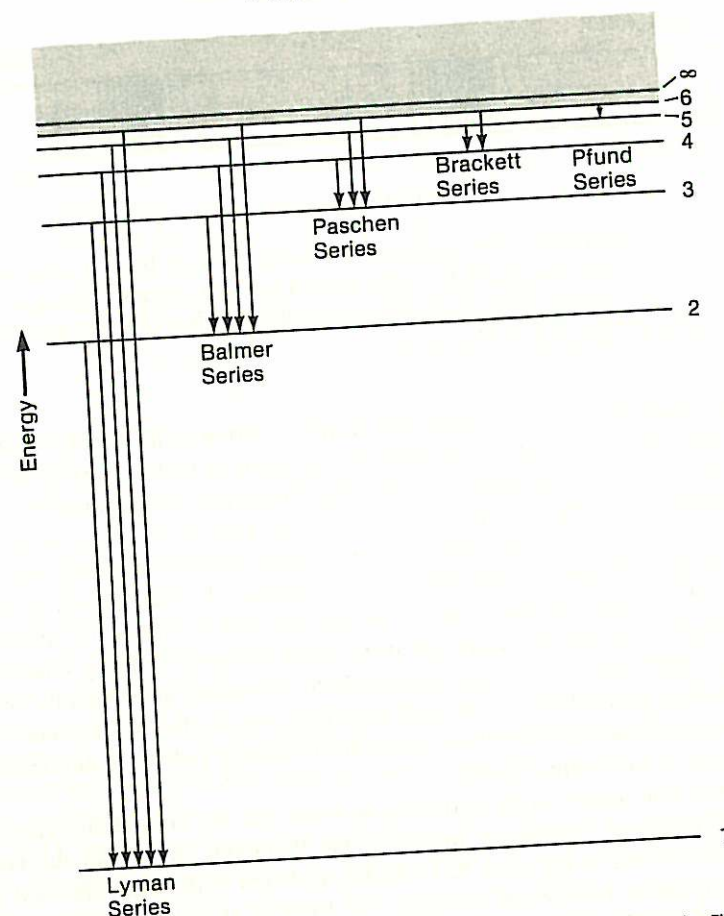


FIGURE 5.9 Energy-level diagram of atomic hydrogen. The series shown in Figure 5.8 are produced by the transitions illustrated here. A single sequence of energy levels serves to predict an infinite number of spectral sequences.

According to Newton's theory, the size and shape of an orbit are determined by two "constants of the motion"—quantities whose value doesn't change as the electron travels along the orbit. One of these is energy; the other (discovered by Johannes Kepler) is called *angular momentum*. An electron's angular momentum is equal to twice the product of its mass and the rate at which an arrow drawn from the nucleus to the electron sweeps out area (Figure 5.10). Angular momentum happens to have the same physical dimension (energy  $\times$  time) as Planck's constant  $h$ . Bohr had the brilliant idea of postulating that the electron in a hydrogen atom must travel in a circular orbit and that its angular momentum must be a whole number of angular-momentum units, an angular-momentum unit being some suitably chosen multiple of Planck's constant (Figure 5.11). This idea worked like a charm. Combined with the Newtonian formula for the energy of an electron

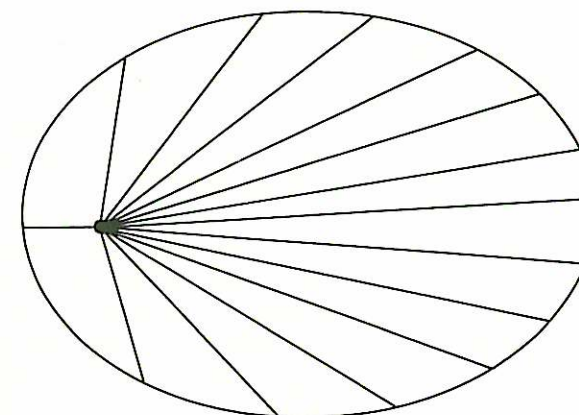


FIGURE 5.10 Kepler's law of areas (conservation of angular momentum). A planet orbiting the Sun sweeps out equal areas in equal times. Radii drawn from the Sun to the planet's position at a sequence of equally spaced moments in time bound sectors of equal area. As a consequence, the planet moves fastest when it is closest to the Sun.

moving in a circular orbit, it yields a formula that exactly reproduces the energy-level diagram illustrated in Figure 5.9, provided the unit of angular momentum is set equal to Planck's constant divided by  $2\pi$ —the ratio of a circle's circumference to its radius. Factors like  $2\pi$  and  $4\pi$  (the ratio of the surface area of a sphere to the square of its radius) are always turning up in the laws of physics, probably because circles and spheres are such basic elements of the mathematical language in which the laws are expressed. So the appearance of the factor  $2\pi$  lent an air of authenticity to the proceedings, like the appearance of a congressman at a clam-bake.

An even more impressive triumph followed shortly. The helium atom has two electrons, and its nucleus has twice the electric charge and four times the mass of the nucleus of a hydrogen atom. At very high temperatures (which spectroscopists can produce for short periods by using electric arcs and sparks), helium atoms part with one of their electrons. A singly ionized helium atom is just like a hydrogen atom except that its nucleus has twice the charge and four times the mass of the hydrogen nucleus, so Bohr could use his theory to predict energy levels of ionized helium. The predictions differed from measured values by less than one-thousandth of 1 percent. Rarely in the history of physics has such a spectacular success been achieved by such simple means.

Bohr's picture of the hydrogen atom resembles Aristarchus's picture of the Solar System. (Aristarchus postulated that the Earth and the five bright planets travel at constant speeds in coplanar circular orbits centered on the Sun.) The two theories are similar in other ways, too. Both rest on ad hoc assumptions; both account for complex phenomena in a surprisingly simple and accurate way; and both served as points of departure for theoretical developments that led eventually to much deeper theories.



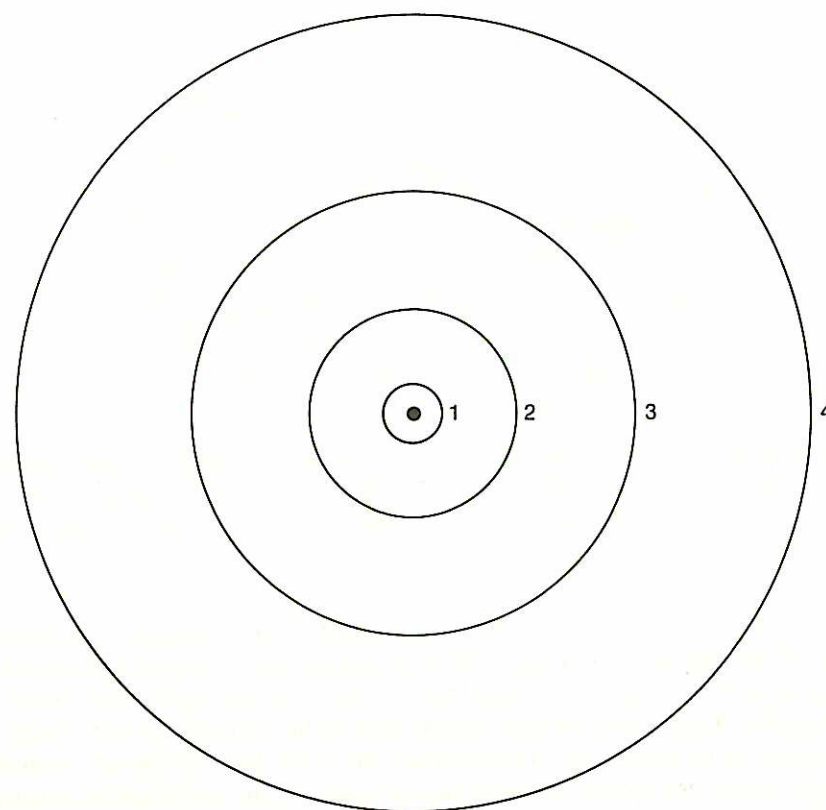


FIGURE 5.11 The first four Bohr orbits. The orbits are circles with radii proportional to  $n^2$ . Thus the four radii are in the ratios 1:4:9:16. The angular momentum of an electron in a Bohr orbit is an integral multiple of Planck's constant divided by  $2\pi$ .

### Step 5: Photons and Quantum Jumps

Having taken a few years off to develop the general theory of relativity, a task completed in 1915, Einstein once more turned his attention to quantum physics. While most of his colleagues were busy exploring the ramifications of Bohr's pioneering study of the hydrogen atom, Einstein characteristically turned his attention to more fundamental problems. His 1917 paper "On the Quantum Theory of Radiation" strengthened the foundation of quantum physics and permanently changed the way physicists view the interaction between light and matter.

In 1905 Einstein had speculated that light might behave as though it consists of discrete particles, and had produced convincing arguments—strongly confirmed by later studies—that the *energy* of monochromatic light of frequency  $f$  can increase or decrease only by whole energy quanta of magnitude  $hf$ . A classical particle has three characteristics: its interactions occur at definite points in space and definite moments in time; it carries a definite energy; and it carries a definite

momentum. (The momentum of a slowly moving classical particle is the product of its mass and its velocity.) In classical physics the energy and momentum of a free particle are simply related. The kinetic energy of a slowly moving particle is equal to the square of its momentum divided by twice its mass, while according to special relativity, a particle of energy  $E$  moving at or close to the speed of light  $c$  has momentum  $E/c$ . Maxwell's theory shows that the same relation holds between the energy and the momentum carried by a beam of monochromatic light. So it was obvious in 1905 that energy quanta in a *parallel beam of light* must also carry momentum and that the energy of an energy quantum is  $c$  times its momentum, as it is for the beam as a whole. Einstein, however, refrained from stating this law until 1917. In the introduction to his 1917 paper he explains why the preceding argument is not airtight:

Let us consider the emission [or light by a molecule] from the point of view of classical electrodynamics. If a body emits the energy  $E$ , it receives a recoil (momentum)  $E/c$  if all the radiation is emitted in the same direction. If, however, the emission takes place isotropically—for instance, in the form of spherical waves—no recoil at all occurs.

In 1905, Einstein hadn't been able to rule out the possibility that energy quanta are emitted isotropically. Twelve years later, he presented a beautiful argument showing that "we arrive at a consistent theory only if we assume each elementary [absorption or emission] to be completely directional." He considered a box filled with radiation and with a gas so dilute that its molecules interact only with the radiation and not with one another, and proved that recoils are needed to maintain the statistical distribution of molecular velocities appropriate to the equilibrium state. The proof relies on a statistical argument that Einstein had used in a famous paper on Brownian motion published in 1905, the year in which his papers on special relativity and energy quanta also appeared.

Einstein had now established that monochromatic light behaves as though it consists of particles (subsequently dubbed *photons*). Still, most physicists didn't accept this conclusion until six years later, when Arthur H. Compton showed experimentally that in interactions between light and electrons, both energy and momentum are exchanged exactly as in a collision between two material particles. Even then, in 1923, several influential physicists—most notably Niels Bohr—still refused to accept the photon hypothesis.<sup>6</sup>

Einstein's 1917 paper not only gave the photon hypothesis a secure theoretical foundation, but also contains what Einstein, in a letter to Michele Besso written in the summer of 1916, describes as "an astonishingly simple derivation of the Planck formula, I might even say *the* derivation. Everything quantal." As we saw earlier, Planck had derived his famous formula by considering the interaction between light and a collection of oscillators. These oscillators were hybrid objects, endowed with contradictory properties. They had discrete energy levels, but radiated and absorbed light in accordance with Maxwell's theory. Einstein put forward a new theory of radiation that made no appeal to Maxwell's theory. He accepted Bohr's postulate that an atom or a molecule has a discrete set of energy



levels and emits or absorbs light only when it makes a jump from one level to another. He then postulated that such jumps are *random processes, governed by statistical laws*. Einstein was ambivalent about this postulate, which marks the entrance of chance on the stage of quantum physics:

The weakness of the [present] theory lies, on the one hand, in the fact that it does not bring any nearer the connexion with the wave theory [of light] and, on the other hand, in the fact that it leaves the moment of occurrence and the spatial direction of the elementary processes [of absorption and emission] to "chance"; all the same, I have complete confidence in the reliability of the method used here.<sup>7</sup>

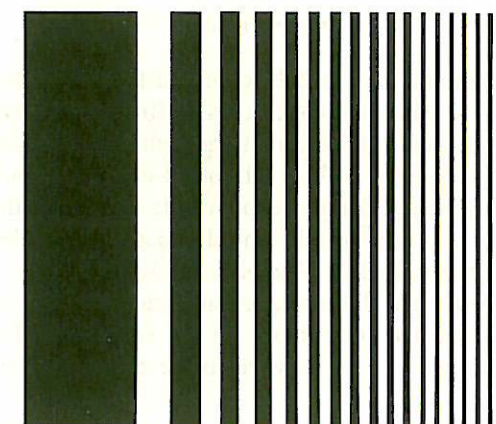
It took physicists another thirty years to explain fully the connection between quantum physics and the wave theory of light, but the second weakness that Einstein perceived in his theory—"that it leaves the moment of occurrence and the spatial direction of the elementary processes [of absorption and emission] to 'chance'"—became a permanent and central feature of quantum physics; chance shed its quotation marks. To the end of his life, however, Einstein resisted the view that chance is inherent in natural phenomena. We will see why in Chapter 6.

### Step 6: Electrons as Waves

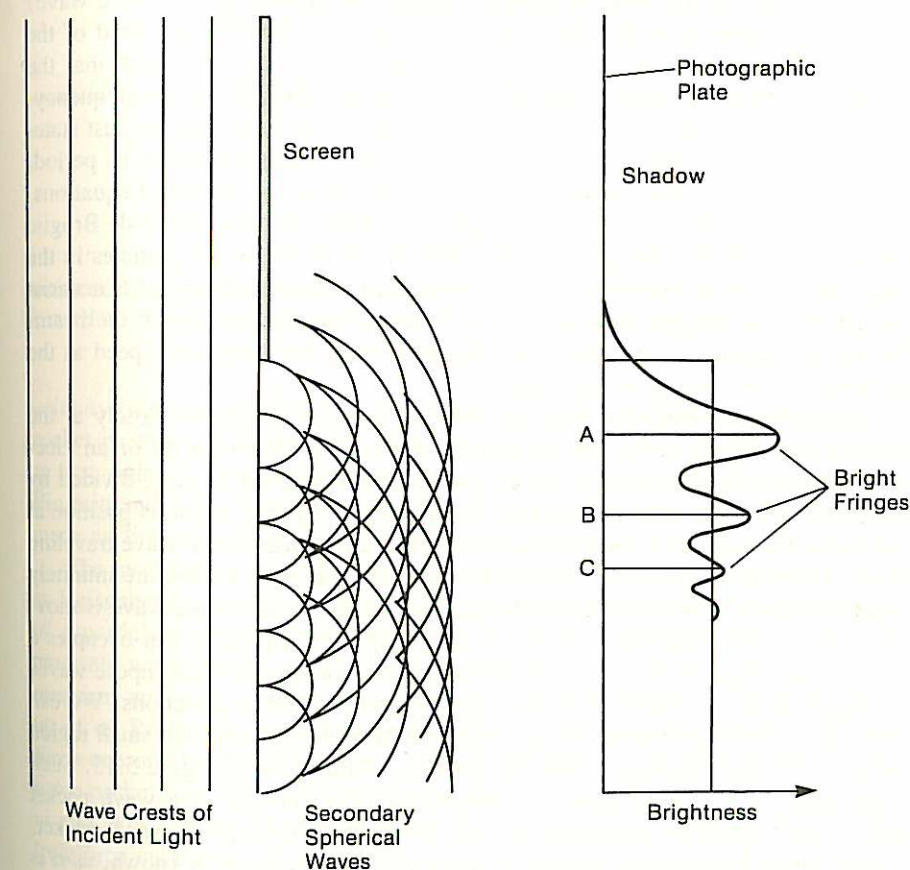
At this point, our path divides. We will follow in the footsteps of Louis de Broglie and Erwin Schroedinger. The other branch was cleared by Werner Heisenberg, Max Born, Pascual Jordan, Paul A. M. Dirac, and Wolfgang Pauli. They reached the summit several months before Schroedinger, but their path is steeper and less direct than the one we will follow, and hard to negotiate without the ropes and pitons of abstract mathematics.

The most characteristic property of a wave—the property that distinguishes it from a beam of particles—is its ability to exhibit *interference*. A sharp-edged screen in the path of a parallel beam of particles casts a sharp-edged shadow; in the path of a parallel monochromatic light wave, it produces a shadow edged with interference fringes (Figure 5.12a). Figure 5.12b illustrates how such fringes are produced when different parts of the same wave that have traveled along slightly unequal paths are reunited.

FIGURE 5.12 (a) An opaque screen in front of a parallel beam of monochromatic light doesn't cast a sharp shadow, because of interference. Instead, a series of closely spaced bright and dark fringes appears at the place where one would expect the edge to be. (b) Every point of the plane that contains the screen, except points on the screen itself, acts as a source of "secondary" spherical waves. These waves arrive at a given point on the photographic plate with different phases because they have traveled different distances. Interference between these secondary waves produces a gradual transition from shadow to light and a series of alternating bright and dark fringes at the edge of the shadow.



(a)



(b)



Shortly after Compton's experiment confirmed that monochromatic light behaves as though it consisted of particles, Louis de Broglie conjectured that a beam of *particles* might, under appropriate conditions, behave like a *wave*. He predicted that a sharp-edged screen in the path of a beam of electrons would cast a shadow edged with interference fringes. Later experiments confirmed this prediction. In 1924, however, direct evidence of this kind didn't yet exist. Electron waves had to be invented before they could be observed.

De Broglie postulated that the frequency and wavelength of an electron beam are related to its energy and momentum by the same formulas that relate the frequency and wavelength of a light wave to the energy and momentum of its photons. Specifically,

$$\text{energy} = h \times \text{frequency} \quad \text{momentum} = h \div \text{wavelength}$$

where, as usual,  $h$  stands for Planck's constant. This may not seem like such a remarkable step. If a light wave behaves, in certain respects, like a beam of particles, why shouldn't a beam of particles behave, in certain respects, like a wave? But there is more to de Broglie's hypothesis than that. How is the speed of the wave related to the speed of the associated particles? You may recall that the speed of a wave is equal to the product of its wavelength and its frequency. (Because the frequency of a vibration is the reciprocal of its period, the last statement is just another way of saying that during a time interval equal to its period, a wave travels a distance equal to its wavelength.) From the displayed equations, we can infer that the product of the frequency and the wavelength of a de Broglie wave, and hence its velocity, is equal to the energy of one of the particles in the beam divided by its momentum. This, however, is *not* the velocity of a material particle. The de Broglie wave moves much faster than the particles in the beam. But for the hypothesis to make sense, the wave must have the same speed as the particles. Or so it seems at first sight.

To resolve this apparent contradiction, we have to look more closely at the relation between electrons and de Broglie waves. By "the velocity of an electron," we mean the distance it travels during a short interval of time, divided by that interval. So we can talk about an electron's velocity only when its position at any given moment has a well-defined value. But a monochromatic wave traveling in a definite direction fills all space. The wave crests of such a wave are infinitely extended parallel planes perpendicular to the direction in which the wave is moving. A monochromatic wave, therefore, can't represent a particle that occupies a tiny volume of space. To represent such a particle, we have to superimpose waves of slightly different wavelengths moving in slightly different directions. We can select these waves in such a way that they reinforce one another in a small region and interfere destructively outside this region, as illustrated in Figure 5.13. Such a collection of waves is called a *wave packet*. The velocity of a wave packet differs from that of its constituent waves, which move *through* the wave packet. If the relation between the speed of a wave and its wavelength is known, as it is for de Broglie waves (because Newton's and Einstein's theories tell us how an electron's energy and momentum are related), it is easy to calculate the velocity of a wave packet. By doing this calculation, de Broglie was able to show that the

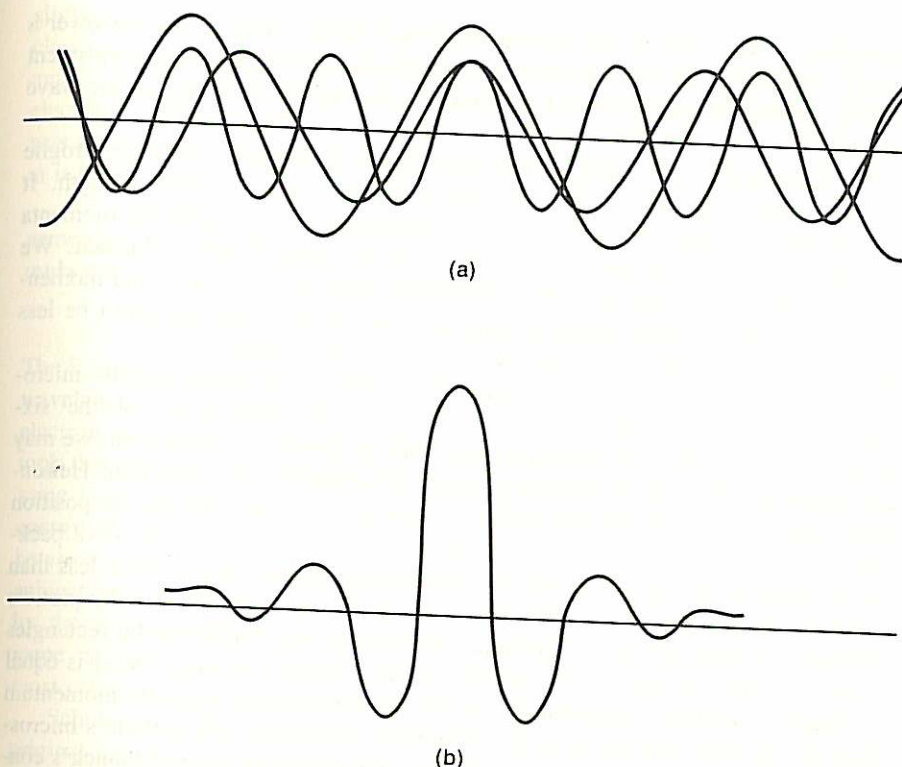


FIGURE 5.13 (a) Representative waves in a wave packet. (b) Profile of the wave packet formed by constructive and destructive interference of the waves that make up the packet.

velocity of a wave packet does indeed coincide with the speed of the particle the packet is supposed to represent. Thus de Broglie's hypothesis, fantastic as it seems at first sight, is internally consistent. This demonstration immediately convinced Einstein and a few others, among them Erwin Schroedinger, that de Broglie had made an important conceptual breakthrough.

The most famous consequence of de Broglie's hypothesis is the statement known as Heisenberg's uncertainty relation, which says that the position and momentum of a particle can't *simultaneously* be known with arbitrary precision. The more precisely we know the particle's position, the less precisely we can know its momentum, and vice versa. A wave packet like that shown in Figure 5.13 is made up of de Broglie waves with a certain range of wavelengths. These waves reinforce one another inside the wave packet and destroy each other outside. Let the wave packet have width  $W$ . Then it contains  $W/w$  de Broglie waves of wavelength  $w$  and  $W/w'$  waves of another wavelength  $w'$ . If the two waves are in phase (reinforce each other) at the center of the wave packet and out of phase (destroy each other) at its edges, these two numbers,  $W/w$  and  $W/w'$ , must differ by a whole number. So they must differ by at least 1. Thus, the spread in the range of reciprocal wavelengths  $1/w$  of the de Broglie waves that make up a wave packet,



multiplied by the width of the wave packet, can't be less than 1. The narrower a wave packet, the greater the spread of the reciprocal wavelengths of its constituent waves; the smaller the spread of reciprocal wavelengths, the broader the wave packet.

Now recall that the momentum of the particle associated with a de Broglie wave is equal to Planck's constant times the wave's reciprocal wavelength. It follows that the width of a wave packet, multiplied by the spread in the momenta associated with its constituent waves, can't be less than Planck's constant. We conclude, finally, that the product of the uncertainties in the position and momentum of the particle whose physical state the wave packet represents can't be less than Planck's constant. This is Heisenberg's uncertainty relation.

We are now, at last, able to justify Boltzmann's assumption that the microstates of particles are represented by finite regions (microcells) of the six-dimensional position-velocity space rather than by points. To begin with, we may use momentum instead of velocity to define a particle's state of motion. Heisenberg's uncertainty relation tells us that a particle's momentum and its position can't both be specified with arbitrary precision. For one-dimensional wave packets, the product of the uncertainties in position and momentum can't be less than Planck's constant. In the two-dimensional position-momentum space of a particle confined to a straight line, the particle's microstates are represented by rectangles whose area (the product of the uncertainties in position and momentum) is equal to Planck's constant. Analogously, in the six-dimensional position-momentum space of a particle that can roam freely in three dimensions, the particle's microstates are represented by cells whose volume is equal to the cube of Planck's constant. The uncertainty principle doesn't restrict the *shape* of a microcell, only its volume.

### Step 7: Stationary Atomic States and Standing Waves

Schroedinger reasoned that if a free electron is represented by a packet of de Broglie waves, the possible state of an electron bound in a hydrogen atom should be represented by standing de Broglie waves with definite frequencies, exactly analogous to the harmonic modes of a vibrating string or drumhead. To test this idea he needed a way to calculate the frequencies of such harmonic modes of vibration.

Most of the waves that physicists had studied were vibrations of a material medium—a string, drumhead, a column of air, or a body of water. Light waves were a recent exception to this rule. From the time of Newton until 1905, physicists had imagined them to be vibrations in a subtle, all-pervading medium, the "luminiferous ether." Einstein's special theory of relativity dispensed with the ether, and eventually physicists stopped believing in it. The standing waves that Schroedinger was trying to describe were presumably of this immaterial kind—vibrations without a vibrating medium.

Water waves, sound waves, and light waves are different species of the same mathematical genus. Each species is governed by a "wave equation" that differs

slightly from the wave equations governing other species. The wave equations of classical physics are themselves consequences of more fundamental laws. For example, the wave equation governing light is a consequence of Maxwell's laws of electromagnetism. Schroedinger, however, couldn't derive the wave equation he was seeking from more fundamental laws because they didn't yet exist. He arrived at it by another route, which I will now try to explain.

All wave equations have a family resemblance, and each is connected by a somewhat complicated but well-understood mathematical transformation to a formula that relates the frequency of the wave to its wavelength:

wave equation  $\leftrightarrow$  relation between frequency and wavelength

The Einstein-de Broglie relations enable us to translate frequency into energy and wavelength into momentum, so we need a formula that relates the *energy* of an electron bound in a hydrogen atom to its *momentum*. Schroedinger, like Bohr, took this formula from classical physics. In fact, Schroedinger and Bohr used the same classical formula, but they used it differently. Bohr used it to express the energy of an electron in a circular orbit; Schroedinger used it to derive a relation between frequency and wavelength for de Broglie waves in a hydrogen atom. By subjecting the resulting equation to the mathematical transformation symbolized by the displayed relation, he derived the famous wave equation that bears his name. Suitably generalized, Schroedinger's wave equation still forms the basis for most calculations in atomic, molecular, and solid-state physics.

Schroedinger himself carried out the first such calculation. He showed that the original equation has standing-wave solutions for only a discrete set of frequencies. These frequencies, translated into energies, coincide exactly with those given by Bohr's theory.

Schroedinger's theory also enabled him to make predictions that lay beyond the reach of Bohr's theory. For example, spectroscopists had discovered that when hydrogen atoms are placed in an electric field, some of their energy levels split into clusters of closely spaced levels. The presence of an electric field adds an extra term to the energy of an electron, which translates into an extra term in the wave equation. Schroedinger was able to solve the modified wave equation and to predict the observed splitting of the energy levels.

\* \* \*

The ascent had been slow and arduous. Rarely could those who led it see beyond the next handhold or foothold. Now broad new vistas opened up on every side, and physicists rushed to stake out their claims. Old sciences like chemistry were taken over and reorganized from top to bottom; new sciences like nuclear physics took root and flourished like weeds. At the same time, the language of quantum physics gradually became more powerful and more abstract. Schroedinger's standing waves came to be seen as one of many equivalent ways of describing the physical state of a bound particle, all of them "representations" of a more abstract mathematical object, the "state vector." Schroedinger himself proved that "wave mechanics"—the theory based on his wave equation and its generalizations—was



mathematically equivalent to “matrix mechanics”—the more abstract theory that had been developed slightly earlier by Heisenberg, Born, Jordan, and Dirac. Physicists discovered that electrons and other particles have internal states that can be described mathematically but can’t be represented spatially, and hence can’t be pictured.

Familiarity and use gradually lent the abstract language of quantum physics an intuitive quality of its own. But now a new difficulty arose. As physicists became more fluent in the new language, they became less certain about what it meant. What was the relation between quantum physics and reality? Quantum physics clearly wasn’t a *picture* of physical reality. What, then, was it? Einstein, Bohr, Heisenberg, and Schroedinger attached great importance to this question, which they answered in different ways. Einstein’s views were the most divergent. Until the end of his life, he remained convinced that quantum mechanics couldn’t be a *complete* description of physical reality. During Einstein’s lifetime, few of his colleagues shared this view. In a letter to Schroedinger in December 1950, Einstein wrote:

You are the only contemporary physicist, besides Laue, who sees that one cannot get around the assumption of reality—if only one is honest. Most of them simply do not see what sort of risky game they are playing with reality—reality as something independent of what is experimentally established. They somehow believe that the quantum theory provides a description of reality, and even a *complete* description. . . .<sup>8</sup>

Many of Einstein’s colleagues believed him to be the victim of philosophical prejudices inherited from the prequantum era—an ironic judgment about the person who, more than anyone else, had been responsible for freeing physics from the view of physical reality underlying classical physics and who had been among the first to recognize and applaud the conceptual breakthroughs of de Broglie and Schroedinger. Since Einstein’s death, however, many physicists have come to recognize that Einstein’s unwillingness to accept quantum physics as a complete description of physical reality was rooted in more than just prejudice. In Chapter 6 we will see why.