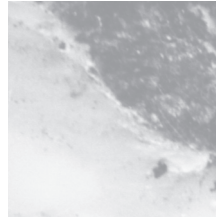


1

Foundations



The tremendous success of Newton's laws of mechanics on scales from footballs to clusters of galaxies is nothing less than staggering. These laws also possess a strong intuitive appeal: the relative ease with which even beginning students can assimilate and apply them is due in no small part to the fact that one can often literally see what the mathematics is describing. Arcing footballs, spinning and colliding billiard balls, rolling tires, flowing water, oscillating pendula, and to some extent even orbiting satellites are the stuff of everyday life and common experience: it's easy to formulate a picture in the mind's eye around which an analysis can be developed. Conversely, quantum mechanics deals with the nature of matter at the atomic level, far removed from the domain of practical experience. Although it now constitutes the foundation of our understanding of everything from the structure of atoms and molecules to the life cycles of stars, it is also often counterintuitive. Its formulation, use, and interpretation are so vastly different from Newtonian mechanics that questions regarding familiar concepts such as position and velocity largely lose their meaning.

The counterintuitiveness of quantum mechanics renders it practically impossible to develop the subject with the smoothness and logical flow of Newtonian mechanics. To a great extent one must simply plunge in and trust that the customs of quantum culture will become familiar as one's experience with it grows. Quantum mechanics is not, however, without its points of contact to classical physics, and these can be exploited to ease the transition to a quantum mode of thinking. The danger in this is that familiar ideas and unquestioned assumptions can be difficult to release; there is an art to sensing how far analogies can be extended. Scientific theories, however revolutionary, do not arise in isolation, and classical mechanics formed the background against which the architects of quantum mechanics constructed their edifice. Qualitatively, quantum mechanics can be viewed as a theory that correctly describes the behavior of microscopic material particles but incorporates the predictions of Newtonian mechanics on macroscopic scales.

The purpose of this chapter is to review some of the facts that led physicists in the early part of the twentieth century to the realization that Newtonian mechanics is invalid in the realm of atomic-scale phenomena. You may have encountered some of the following material in an earlier course: the experiments of Michael Faraday and

J.J. Thomson (Section 1.1), the nature of atomic spectra (Section 1.2), the Rutherford-Bohr model of the atom (Section 1.3), and wave-particle duality (Section 1.4). The intention here is not in-depth explanation, but rather the context of early twentieth-century physics and the discrepancies between experiment and theory that forced the development of a whole new area of physics.

■ 1.1 Faraday, Thomson, and Electrons

The roots of modern scientific speculation on atomic structure trace their origins to the early nineteenth century. From the chemical experiments of Antoine Lavoisier and John Dalton, the concept of an atom as the smallest unit representative of a given element was firmly established by about 1810. Michael Faraday's electrolysis experiments of the early 1830s suggested that electrical current involved the transport of "ions," which were what we now recognize as individual atoms or molecules bearing net positive or negative electrical charges. Faraday thus perceived that nature **quantizes** certain quantities: ions could apparently not possess any arbitrary amount of electrical charge, but rather only integral multiples of a fundamental unit of charge. In 1881 Irish physicist George Stoney [1] first estimated the fundamental unit of negative charge to be about -10^{-20} Coulomb. In 1891, he coined the term "electron" to describe the carriers of the fundamental unit of negative charge.

Knowledge of Avogadro's number, along with knowledge of the density and atomic weight of an element, makes it possible to estimate the effective sizes of atoms constituting that element. If one imagines a substance to be composed of tightly-packed spherical atoms of radius R , the distance between atomic centers will be $2R$. Each atom will effectively occupy a volume of space equivalent to a cube of side length $2R$, namely $8R^3$. If the atomic weight of the substance is A grams per mole, the mass of an individual atom will be A/N_A and the density will be $\rho = A/8N_AR^3$, which we can turn into an expression for the atomic radius:

$$R = \left(\frac{A}{8N_A\rho} \right)^{1/3}. \quad (1)$$

By applying Equation (1) to light and heavy elements, we can get an idea of the range of atomic sizes. At one extreme is lithium, the lightest naturally solid element. With $A = 7$ gram/mole (1.1×10^{-26} kg/atom) and $\rho = 0.534$ gram/cm³, we find $R \sim 1.40 \times 10^{-10}$ meter, or 1.40 \AA ($1 \text{ \AA} = 10^{-10}$ meter). At the other end of the periodic table is uranium, the heaviest naturally occurring element, with $A = 238$ gram/mole (4×10^{-25} kg/atom) and $\rho \sim 18.95$ grams/cm³, which give $R \sim 1.38 \text{ \AA}$. Despite a factor of 80 difference in mass, uranium and lithium atoms effectively act

as if they are about the same size! This is a simplistic analysis, but it does demonstrate the chemical wisdom that essentially all atoms act as if they are on the order of 1 \AA in radius. The Ångstrom is a convenient unit of length for atomic-scale problems and will be used extensively throughout this text.

In 1897, J. J. Thomson [2] undertook his famous cathode-ray deflection experiments (“cathode ray” was an early term for electron), from which he determined the charge-to-mass ratio (e/m) of the electron. In modern units he arrived at a value of about -2×10^{11} coulombs/kg; in combination with Stoney’s charge estimate of $\sim -10^{-20}$ coulomb, it became clear at once that the mass of the electron must be on the order of 10^{-31} kg, some four orders of magnitude smaller than atomic masses. Moreover, Thomson found the same result for a variety of different cathode materials, demonstrating that electrons are universal constituents of all atoms.

At the time of Thomson’s e/m experiments, Robert Millikan’s oil drop experiments to precisely determine the value of e lay well in the future (1909). However, let us break with historical sequence to make a point about the size of the electron itself. We begin with the modern values for the mass and charge of the electron:

$$m_e = 9.10954 \times 10^{-31} \text{ kg},$$

and

$$e = -1.60219 \times 10^{-19} \text{ C}.$$

Now, a common demonstration in elementary texts on electricity and magnetism is the derivation of an expression for the self-potential-energy V of a solid sphere of radius r bearing an electrical charge e distributed uniformly throughout. The result is

$$V = \frac{3e^2}{20\pi\epsilon_0 r}. \quad (2)$$

If we assume that this self-energy is equivalent to the sphere’s Einsteinian rest energy $E = mc^2$ (another break from historical sequence: Einstein did not develop his special theory of relativity until 1905), we can solve for the radius of the sphere:

$$r = \frac{3e^2}{20\pi\epsilon_0 mc^2}. \quad (3)$$

For an electron the numbers give

$$r_e = \frac{3(-1.602 \times 10^{-19} C)^2}{20\pi(8.85 \times 10^{-12} C^2/Nm^2)(9.11 \times 10^{-31} kg)(2.998 \times 10^8 m/s)^2}$$

$$= 1.69 \times 10^{-15} m \sim 10^{-5} \text{ atomic radii.}$$

Electrons are minute in comparison to their host atoms; essentially, they are point masses. Actually, the current experimental evidence is that electrons are in fact point masses, and that protons have radii of about $0.8 \times 10^{-15} m$.¹ The preceding analysis predicts a radius of $\sim 10^{-18} m$ for the proton; we can interpret the discrepancy as indicating that the origin of mass cannot purely be energy. (This is not to imply that $E = mc^2$ is somehow in error, only that this approach cannot be an adequate model for the origin of mass. Modern versions of quantum field theory hold that mass is built up of particles known as quarks and gluons and fields that connect them.)²

Considerations along these lines stimulated development of models of atoms wherein pointlike, negatively charged electrons were held in stable configurations by their mutual repulsion within a larger positively charged cloud; Thomson himself was one of the prime movers in this effort. (Atomic model-building had a venerable history well before Thomson; an engaging account is given by Pais [3].) However, these efforts met with little success, for they failed to explain atomic and molecular spectra. In addition, Thomson's 1898 atomic model proved of no value in explaining the continuous spectrum of blackbody radiation. These phenomena played pivotal roles in the development of quantum mechanics.

■ 1.2 Spectra, Radiation, and Planck

In 1814, German scientist Joseph Fraunhofer passed sunlight through a prism and examined the resulting continuous spectrum of colors with a magnifying glass. To his surprise, he observed hundreds of dark lines crossing the spectrum at specific wavelengths. Later, in the 1850s, Gustav Kirchoff observed the same effect on passing light from artificial sources through samples of gas. Work along these lines culminated in Kirchoff's three law of spectroscopy:

1. Light from a hot solid object, on passing through a prism, yields a continuous spectrum with no lines.

¹*Physics Today* 1995; 48(11):9

²*Physics Today* 1999; 52(11):11 and 2000; 53(1):13.

2. The same light, when passed through a cool gas, yields the same continuous spectrum but with certain wavelengths of light removed, a so-called absorption spectrum.
3. If the light emitted by a hot gas alone is viewed through a prism, one observes a series of bright lines at certain wavelengths superimposed on an otherwise black background, a so-called emission spectrum.

The key observation was that if the same gas is used in (2) and (3), the absorption and emission lines appear at the same wavelengths in both cases. These phenomena are illustrated schematically in Figure 1.1.

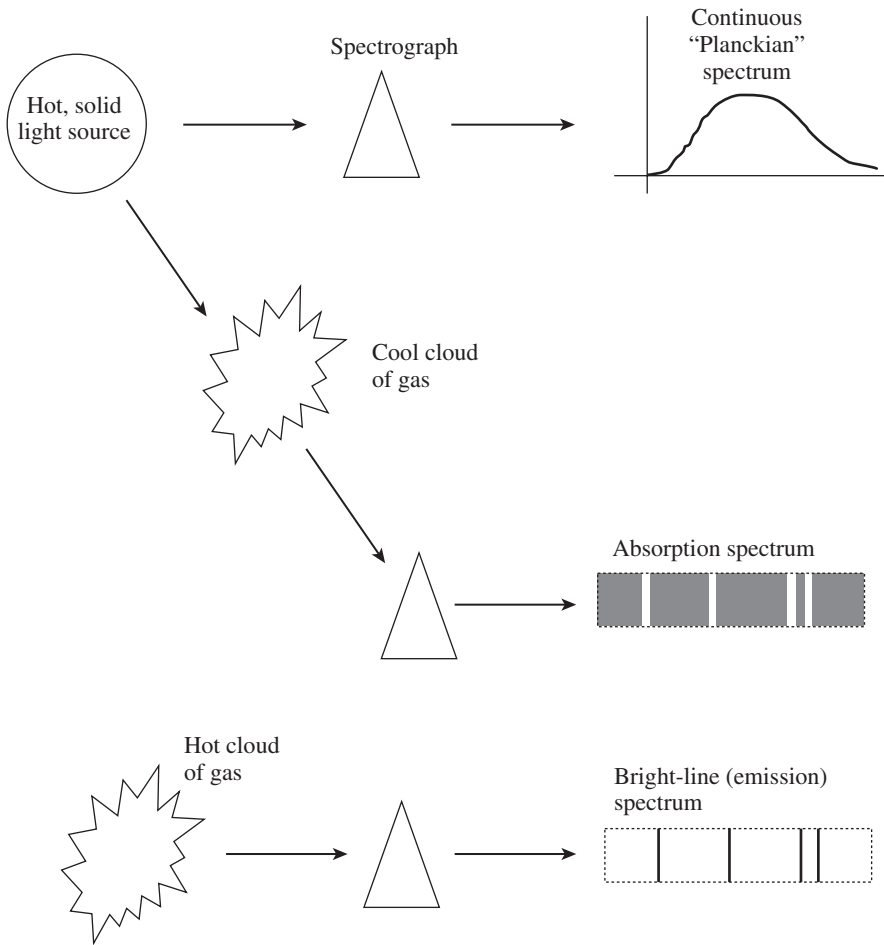


FIGURE 1.1 Kirchoff's Laws.

It soon became clear that every chemical element or compound produces a characteristic pattern of spectral lines; spectroscopy serves as a diagnostic test for the presence or absence of an element or compound in a given sample. Spectra of a few substances are shown in Figure 1.2 (reproduced from [4]). Hydrogen displays the simplest pattern of any element: a series of lines separated by ever-decreasing gaps until a “continuum” of emission is reached at a wavelength of about 3646 Å. Molecular spectra are characterized by overlapping patterns of lines, but regularities are still apparent.

Explaining line spectra posed a tremendous challenge to builders of atomic models. Because Maxwell’s equations revealed that an accelerating electrical charge radiates energy in the form of light, it was logical to suggest that spectral lines arise from the motion of Thomson’s “corpuscular” electrons in the vicinity of whatever constitutes the massive, positively charged part of the atom. Thomson proposed an atomic model consisting of pointlike electrons embedded within a much larger spherical cloud of positive charge, the so-called “raisin bread” or “plum-pudding” model. In such an arrangement the electrons will oscillate back and forth through the cloud in simple harmonic motion as would a billiard ball dropped into a frictionless hole bored through the Earth. Although these oscillations lead to frequencies on the order of that of visible light, Thomson’s model suffers from two serious difficulties. The first is that only one frequency results from an atom of a given size. How are we to account for whole series of spectral lines? The second difficulty is even more catastrophic. As the electron radiates away energy the amplitude of its motion should steadily decrease until it comes to rest in the center of the atom. In short, matter should collapse!

How, then, to explain discrete-line spectra at all? Thomson worked with immense dedication over many years on a variety of models of this general sort, but with no real success. Understanding the stability of atoms and the origin of line spectra had to await the augmentation of classical models by new quantum postulates.

There was, however, one piece of evidence that gave early atomic theorists hope that nature might yield her secrets to mathematical analysis. In 1885, Johann Balmer discovered that the spectral lines of hydrogen followed a simple mathematical regularity [5], namely, that they could be computed from the formula

$$\lambda_n = 3646 \left(\frac{n^2}{n^2 - 4} \right) \text{Å}, \quad n = 3, 4, 5, \dots \quad (1)$$

Note that as $n \rightarrow \infty$, $\lambda^n \rightarrow 3646 \text{ Å}$, the wavelength at which the hydrogen spectral lines “pile up” into a continuum.

Balmer’s formula was purely empirical, with no model of an underlying physical mechanism. This does not diminish its value, though, for when a phenomenon can be

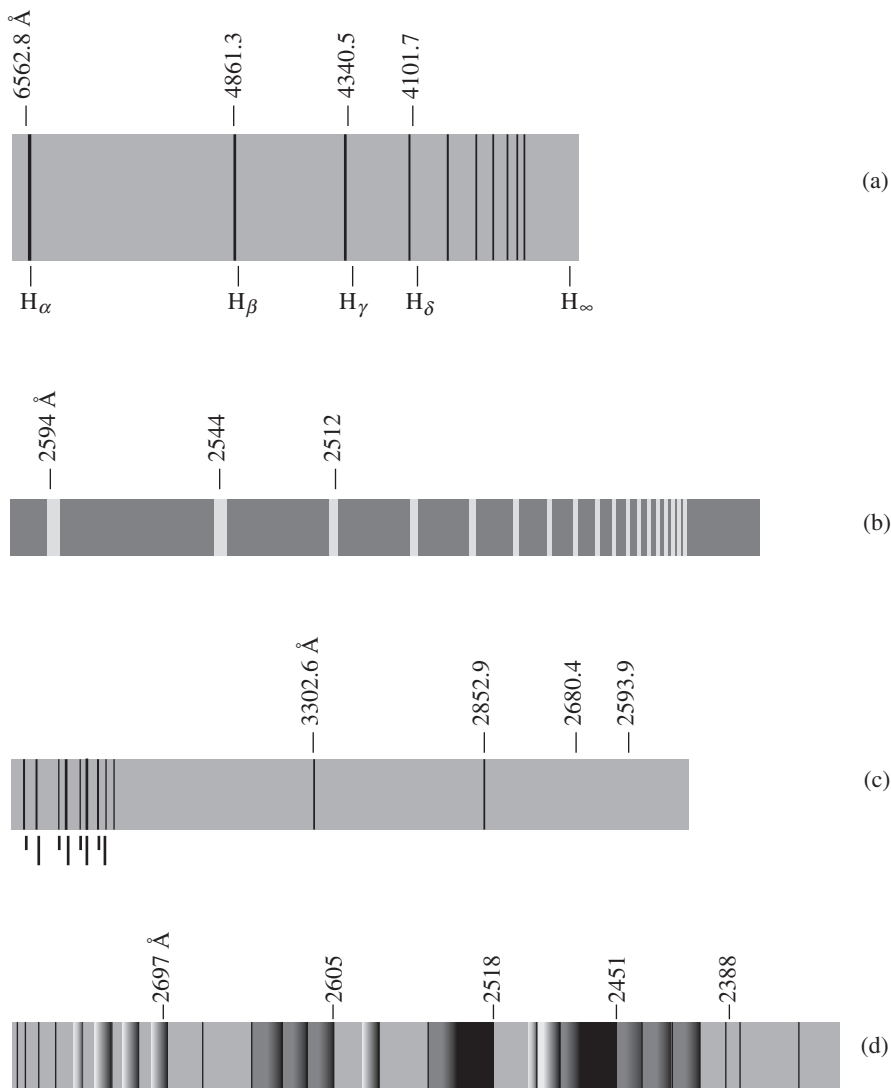


FIGURE 1.2 (a) Emission spectrum of hydrogen.
 (b) Absorption spectrum of sodium.
 (c) Emission spectrum of sodium.
 (d) Spectrum of PN molecule.

Reproduced from G. Herzberg, *Atomic spectra and atomic structure*, Dover Publications, Inc., New York, 1944. Reprinted through the permission of the publisher.

fitted into a simple arithmetic scheme one is justified in having hope that a deeper understanding may not be far off. Indeed, Balmer's formula was a key clue for Niels Bohr's development of the first really successful theory of atomic structure.

We remark in passing that spectroscopists often refer to spectral lines by their reciprocal wavelengths. Balmer's formula can be rearranged to reflect this:

$$\frac{1}{\lambda_n} = R_H \left(\frac{1}{4} - \frac{1}{n^2} \right) \text{\AA}^{-1}, \quad n = 3, 4, 5, \dots, \quad (2)$$

where R_H is known as the *Rydberg constant* for hydrogen; its experimental value is $109,678 \text{ cm}^{-1}$. With considerable success, Swedish physicist Johannes Rydberg suggested that the spectral lines of any element could be described by a generalized version of Equation (2):

$$\frac{1}{\lambda_{n,m}} = K \left(\frac{1}{m^2} - \frac{1}{n^2} \right) \quad (n > m), \quad (3)$$

where K is a constant specific to the element involved. Different series of spectral lines are given by various values of n for a fixed value of m . We will return to this modified Balmer formula later in this chapter.

Continuous spectra also posed a challenge to classical physics. Experimentally, any solid body at a temperature T above absolute zero emits a continuous spectrum of electromagnetic radiation. By the end of the nineteenth century, experiment had also established that the spectrum of "thermal radiation" emitted by a body is independent of the nature of the body, depending only on T . These experiments were usually carried out with so-called "blackbody" cavities. This can be thought of as a heated, internally hollow lump of metal with a hole in it from which some of the thermal radiation can escape and so be sampled by a detector. Figure 1.3 shows spectra for the light emitted by such cavities at temperatures of 5000, 6000, and 7000 K over the wavelength range 2000–10,000 Ångstroms; what is plotted is the power emitted per square meter of surface area of the sampling hole per unit Ångstrom wavelength interval as a function of wavelength. (The range of human vision spans approximately 3500–7000 Å). As T increases, the wavelength of peak emission shifts to shorter (bluer) wavelengths. If you are familiar with some stellar astronomy, you may know that blue stars have hotter surfaces than yellow stars, which in turn are hotter than red-dwarf stars.

Attempts to find a mathematical description of thermal radiation based on classical models failed completely. The generally held concept was somewhat analogous to Thomson's oscillating electrons: each atom of a material body would be in constant motion, jostling about with its neighbors. When a charged particle oscillates at

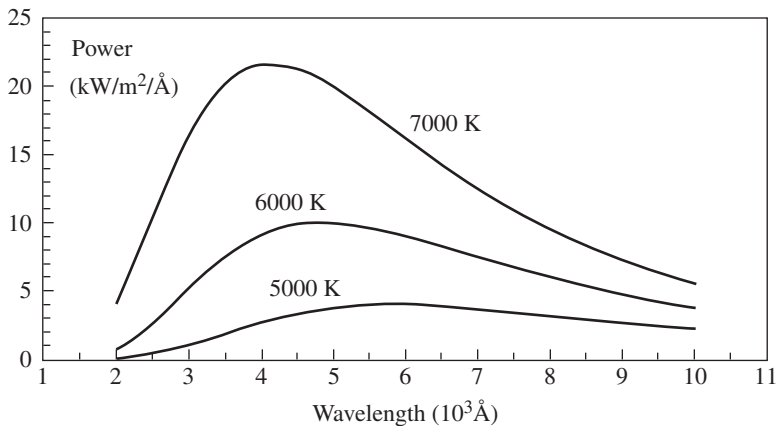


FIGURE 1.3 Thermal Radiation Spectra.

frequency ν (in, say, simple harmonic motion as studied in freshman-level physics classes), it will emit electromagnetic radiation at that same frequency; for this reason the atoms were abstracted as “oscillators.” (Recall that, in 1900, knowledge of the detailed internal structure of atoms was essentially nil.) The cavity will fill with electromagnetic radiation bouncing around at the speed of light, and an equilibrium (“thermal equilibrium”) will soon be established as the oscillators emit and absorb radiation. Like standing waves on a vibrating string, however, the cavity can only “support” electromagnetic waves of certain frequencies, depending on its dimensions. From Maxwell’s theory, the number of possible “standing-wave” frequencies available between frequencies ν and $\nu + d\nu$, usually designated as $N(\nu)d\nu$ was given by

$$N(\nu)d\nu = \frac{8\pi V}{c^3} \nu^2 d\nu, \quad (4)$$

where V is the volume of the cavity and c is the speed of light. An approximate derivation of this expression is given in Section 6.1. Now, what is desired is an expression for the energy within the cavity (in the form of electromagnetic waves) in some specified range of frequencies: this is what the measurements ultimately sample. In effect, we need to know how many oscillators are oscillating at each available frequency and what amount of energy is associated with each mode of oscillation. In classical physics, however, there is no connection between the energy of an oscillator and its frequency. You can set the amplitude and frequency of a vibrating string separately to be whatever values you please. To build a connection to energy, the approach

adopted was to appeal to the success of Maxwell and Boltzmann's work on statistical mechanics. Their research showed that if a particle is in an environment at absolute (Kelvin) temperature T , then the probability of it's having energy between E and $E + dE$ is proportional to an exponential function of T :

$$p(E)dE = A e^{-E/kT} dE, \quad (5)$$

where A is a constant and k is Boltzmann's constant. To determine A we insist that if we add up probabilities over all possible energies they must sum to unity. This is equivalent to saying that the particle must have *some* energy between 0 and infinity. That is, we demand

$$\int_0^{\infty} p(E)dE = A \int_0^{\infty} e^{-E/kT} dE = 1.$$

This integral evaluates to kT , giving $A = 1/kT$. The *average* energy of a particle in such a situation is then given by the integral of probability-weighted energy:

$$\langle E \rangle = \int_0^{\infty} E p(E)dE = \frac{1}{kT} \int_0^{\infty} E e^{-E/kT} dE = kT. \quad (6)$$

(For a fuller elaboration of this averaging technique, see Section 4.2.) The assumption is now made that the number of oscillators wiggling about with frequencies between ν and $\nu + d\nu$ is given by Equation (4), and that the amount of radiant energy in the cavity between these frequencies is consequently given by this number times the average energy of an oscillator at temperature T , kT :

$$E(\nu)d\nu = \frac{8\pi V}{c^3} kT \nu^2 d\nu. \quad (7)$$

Despite these various assumptions, this relationship actually proved to be in good agreement with experimental data at low frequencies. At high frequencies, though, one has a disaster: The amount of energy in the cavity becomes infinite, a situation known as the ultraviolet catastrophe. Something was apparently wrong with either classical electromagnetism or statistical mechanics, or perhaps even both. It is probably fair to say that at the dawn of the twentieth century, thermal radiation was *the* outstanding problem of theoretical physics.

A way around this difficulty was found by Max Planck of the University of Berlin in late 1900, in a paper usually credited with marking the birth of quantum mechanics proper [6]. However, his solution came at a substantial price: abandoning the classical notion that the energy and frequency of an oscillator are independent. Planck proposed

that the energy of an oscillator is restricted to only certain multiples of its frequency, namely, $E_n = nh\nu$, where n is an integer-valued “quantum number” ($n = 0, 1, 2, 3, \dots$) and h is a constant of nature.

Maintaining the assumption of a Maxwellian exponential probability distribution, the probability of an oscillator having energy E is now given by

$$p(E) = Ae^{-nh\nu/kT}, \quad (8)$$

where A is again a normalization constant. Note carefully that no “ dE ” appears in this expression: the idea now is that an oscillator has some probability of having a *particular* energy, as opposed to any arbitrary energy between E and $E + dE$. Forcing the probabilities to again add up to unity means that we must have

$$A \sum_{n=0}^{\infty} e^{-nh\nu/kT} = 1,$$

or

$$A \sum_{n=0}^{\infty} (e^{-h\nu/kT})^n = 1. \quad (9)$$

We are summing over *discrete* energy states as opposed to integrating over energy as a *continuous* variable. The sum appearing in Equation (9) is of the form $\sum x^n$, where $x = e^{-h\nu/kT}$; that is, we have a geometric series. Such a sum evaluates to $(1 - x)^{-1}$, hence

$$A = (1 - e^{-h\nu/kT}), \quad (10)$$

and so the probability of an oscillator having energy E can be written as

$$p(E) = e^{-nh\nu/kT}(1 - e^{-h\nu/kT}). \quad (11)$$

With this new probability recipe, the average energy of oscillators of frequency ν becomes

$$\begin{aligned} \langle E \rangle &= \sum_{n=0}^{\infty} E p(E) = \sum_{n=0}^{\infty} (nh\nu) p(E) = h\nu(1 - e^{-h\nu/kT}) \sum_{n=0}^{\infty} ne^{-nh\nu/kT} \\ &= h\nu(1 - e^{-h\nu/kT}) \frac{e^{-h\nu/kT}}{(1 - e^{-h\nu/kT})^2} = \frac{h\nu}{(e^{h\nu/kT} - 1)}. \end{aligned} \quad (12)$$

In working Equation (12), we have used another result from series analysis, namely

$$\sum_{n=0}^{\infty} n x^n = \frac{x}{(1-x)^2} \quad (|x| < 1),$$

where we again have $x = e^{-h\nu/kT}$. Again assuming that the number of oscillators with frequencies between ν and $\nu + d\nu$ is given by Equation (4), we find a new expression for the energy in the cavity between frequencies ν and $\nu + d\nu$:

$$E_\nu d\nu = \frac{8\pi hV}{c^3} \frac{\nu^3}{(e^{h\nu/kT} - 1)} d\nu. \quad (13)$$

This is Planck's famous **blackbody radiation formula**. Note that frequency is still a *continuous* variable; the energy that an oscillator can have is *discretized* by $E = nh\nu$ once its frequency is specified. Planck found this expression to be a perfect match to the experimental data provided that the constant h is chosen suitably. This quantity is now known as **Planck's constant** and has the value

$$h = 6.626 \times 10^{-34} \text{ Joule-sec.}$$

Planck's assumption is now practically an element of popular culture. Hindsight tends to blind us to perceiving just how radical it was to his contemporaries. That electrical charges come in discrete units is one thing, but to suggest that the most venerable quantity in all of physics, energy itself, could be exchanged only in discrete lumps—in other words, that it is **quantized**—was to disavow two and a half centuries of accumulated wisdom. As with all fundamental postulates, the difficulty in understanding it and its consequences stems from just that: like $\mathbf{F} = m\mathbf{a}$ it is a postulate, not derivable from anything more fundamental. The justification for Planck's hypothesis is that it has never been found to lead to conclusions in conflict with experiment.

The development of blackbody theory actually spanned the better part of two decades, with Planck modifying his assumptions and calculations many times; the preceding description represents only a very cursory survey of the issue.³

Planck's hypothesis lay essentially dormant until 1905 when Einstein adapted it to explain the photoelectric effect, the emission of electrons from a metal surface being bombarded by light [7]. This phenomenon had proven impossible to understand when light was considered as a wave (as in the Maxwellian tradition), but became clear if the light were regarded instead as a stream of particles (**light-quanta** or **photons**) of energy $E = h\nu$, where ν is the frequency of the wave one would normally

³Readers interested in exploring more deeply this fundamental revolution in physics are directed to Thomas Kuhn's comprehensive *Black-Body Theory and the Quantum Discontinuity, 1894–1912*. Chicago: University of Chicago Press, 1978.

associate with the light. It was as if the incident light were colliding billiard-ball style with electrons, knocking them out of the metal. Although Einstein's work resolved the photoelectric effect, it thrust into the foreground an apparent paradox: Is light a wave or a stream of particles? On one hand it behaves optically as any sensible wave: it is refractable, diffractable, focusable, and so forth. On the other it can behave dynamically, like billiard balls. Which picture do we adopt? The answer is, "We have to live with both." Although in some circumstances one can conveniently analyze an experiment with an explicitly wave picture in mind (for example, double-slit diffraction in classical optics), whereas in others a particle view provides for a convincing analysis (the photoelectric effect), the inescapable fact is that photons possess both wave and particle properties simultaneously (as material particles such as electrons and entire atoms and molecules—see Section 1.4). Indeed, it has been amply experimentally verified that photons interfere with themselves even as they pass, one by one, through an optical system!⁴ We shall have more to say about this wave-particle duality in coming chapters.

The idea of light carrying momentum was not new during the early part of the twentieth century. Indeed, Maxwell had predicted that electromagnetic radiation of energy E would possess momentum in the amount $p = E/c$. (If you are familiar with special relativity, recall the Einstein energy-momentum-rest mass relation $E^2 = p^2c^2 + m_0^2c^4$, and set the rest mass m_0 to be zero for a photon.) This can be expressed in terms of the frequency of the light as $p = E/\lambda$ since $c = \lambda\nu$. If light is also treated as consisting of particles characterized by the Planck relation $E = h\nu$, then $p = h/\lambda$ or

$$\lambda = \frac{h}{p}. \quad (14)$$

Equation (14) applies only to photons even though it was derived from a mixture of both classical and quantum concepts. Nevertheless, in the 1920s, Arthur H. Compton verified that photons and electrons indeed interact billiard-ball style, precisely as the equation predicts. This deceptively simple equation will figure in subsequent discussions.

The substitutions leading to Equation (14) are simple. Yet, it seems remarkable that the connection between Planck's quantized oscillator energies and the discrete wavelengths (= discrete energies) of light constituting spectral lines was not made for nearly another decade. This breakthrough had to await further experimental probing of the internal structure of atoms.

⁴For readers interested in learning about the details of such experiments and many other aspects of the fundamentals of quantum mechanics, George Greenstein and Arthur Zajonc's *The Quantum Challenge* (Sudbury, MA: Jones & Bartlett, Second Edition, 2006) is highly recommended.

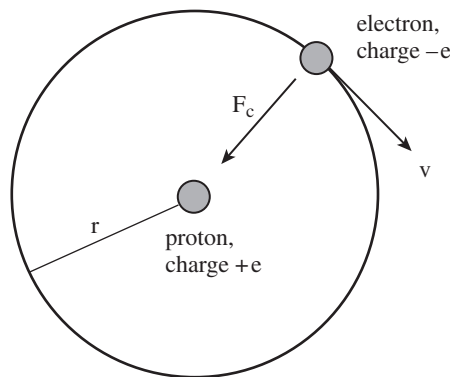
■ 1.3 The Rutherford-Bohr Atom

In early 1911, Ernest Rutherford, in collaboration with Hans Geiger and Ernest Marsden, proposed a model of atomic structure radically different from Thomson's plum-pudding scenario [8]. Based on an analysis of the distribution of alpha-particles (helium nuclei) scattered through thin metal foils, they put forth a **nuclear** model of the atom wherein the positive charge (and with it most of the atomic mass) is concentrated in a tiny volume of space at the center of the atom, around which negative electrons orbit like planets about the Sun.⁵ Their experiments indicated a size on the order of 10^{-14} meters for the positively charged nucleus: it was larger than an electron, but some four orders of magnitude smaller than the atom itself. Evidently, atoms are mostly empty space.

The stage was now set for a leap of logic of the sort alluded to at the end of Section 1.2. Planck had established that atoms constituting the source of thermal radiation from material bodies could exist only in certain discrete energy states. If Rutherford's planetary electrons were restricted to orbits of certain special energies, could electrons "transiting" from orbits of higher energy (say, E_2) to orbits of lower energy (say, E_1) be the source of spectra and thermal radiation, with the energy difference appearing as a photon of frequency ν_{21} given by Planck's hypothesis written in the form $E_2 - E_1 = h\nu_{21}$? These were among the assumptions made by a young Danish physicist, Niels Bohr, in a trilogy of papers published in the *Philosophical Magazine* in 1913 that marked the first truly successful theory of the inner workings of atoms [9].

Let us explore the consequences of Bohr's postulates for a simple model of the hydrogen atom. The situation is illustrated in Figure 1.4, where an electron of mass m_e

⁵An excellent website on the life and work of Rutherford can be found at www.rutherford.org.nz.



■ FIGURE 1.4 Bohr Model for Hydrogen.

and charge $-e$ is in a circular orbit of radius r and speed v around a central proton of charge $+e$.

Bohr began by assuming that the energetics of the electron's orbit are dictated by the Newtonian dynamics of circular orbits, namely that if the electron is in a circular orbit, then it must experience a centripetal force of magnitude $m_e v^2/r$ toward the proton. Identifying as the source of this centripetal force the Coulomb attraction between electron and proton gives

$$\text{magnitude of Coulomb force} = \frac{m_e v^2}{r} = \frac{e^2}{4\pi\epsilon_0 r^2}. \quad (1)$$

A more refined version of this calculation accounts for the motion of the proton and the electron about their mutual center of mass. This can be effected by substituting the reduced mass of the system, $m_e m_p / (m_e + m_p)$ in place of the electron mass m_e wherever it appears; m_p is the mass of the proton. Also, the theory can be extended to include hydrogen-like ions; that is, systems wherein a single electron orbits a nucleus of charge $+Ze$, by replacing e^2 by Ze^2 wherever it appears.

Because the physically relevant quantities are wavelengths and energies, we start out by deriving an expression for the total energy (kinetic + potential) of the electron in its orbit. From Equation (1),

$$\text{Kinetic energy} = \frac{1}{2} m_e v^2 = \frac{e^2}{8\pi\epsilon_0 r}. \quad (2)$$

The potential energy is just the electrostatic potential of an electron (charge $-e$) and a proton (charge $+e$) separated by distance r :

$$\text{Potential energy} = -\frac{e^2}{4\pi\epsilon_0 r}. \quad (3)$$

From Equations (2) and (3) we find the total energy E_{total} :

$$E_{\text{total}} = \text{KE} + \text{PE} = -\frac{e^2}{8\pi\epsilon_0 r}. \quad (4)$$

The interpretation of the negative sign is that positive energy must be supplied from some external source to dissociate the electron from the atom. We say that the electron is in a **bound energy state**. Curiously, the total energy is equal to one-half of the potential energy; this result is actually a specific case of a very general result known as the **virial theorem**, which is treated in Section 4.9.

Imagine the electron "falling" from infinity [$E = 0$ with $r = \infty$ in Equation (4)] down to an orbit of radius r about the proton. In doing so it would lose energy,

which is assumed to appear as a photon of frequency ν . At this point, Bohr made two assumptions: (1) that this frequency is equal to one-half of the electron's final orbital frequency about the proton, and (2) consistent with Planck's hypothesis, the energy of the photon is given by $nh\nu$ where n is an integer and h is Planck's constant. For an electron in a circular orbit of speed v and radius r , the time for one orbit is $2\pi r/v$, hence the orbital frequency is $v/2\pi r$ and Bohr's hypotheses give

$$E_{\text{photon}} = |E_{\text{total}}| = nh\nu = \frac{nh}{2} \left(\frac{v}{2\pi r} \right) = \frac{e^2}{8\pi\epsilon_0 r}. \quad (5)$$

Solving the last two members of this expression for v gives

$$v = \frac{e^2}{2\epsilon_0 nh}. \quad (6)$$

Now solving Equation (2) for the orbital radius and substituting this result for v gives

$$r_n = \left(\frac{\epsilon_0 h^2}{\pi m_e e^2} \right) n^2 = a_0 n^2, \quad (n = 1, 2, 3, \dots). \quad (7)$$

The interpretation of equation (7) is that the electron is restricted to orbits of radius $a_0 n^2$, where a_0 , now known as the **Bohr radius**, represents the smallest permissible orbit (note that we cannot have $n = 0$, for this would imply $E = -\infty$ in equation 4); n is called the **principal quantum number**.

Using the following modern values for the constants

$$\epsilon_0 = 8.8542 \times 10^{-12} \text{C}^2/\text{Nm}^2,$$

$$h = 6.6261 \times 10^{-34} \text{J-sec},$$

$$m_e = 9.1094 \times 10^{-31} \text{kg},$$

$$e = 1.6022 \times 10^{-19} \text{C},$$

one finds

$$a_0 = 5.2918 \times 10^{-11} \text{ m} = 0.52918 \text{ \AA}. \quad (8)$$

This is a remarkable result, exactly of the order of atomic dimensions as deduced in Section 1.1. Bohr's assumptions result in a theoretical explanation of the sizes of atoms, an otherwise empirical detail.

EXAMPLE 1.1

The lone proton in a hydrogen atom has an effective radius of about 10^{-15} m. Suppose that the entire atom is magnified so that the proton has a radius of 1 mm, about the size of a rather small pea. If the orbiting electron is in the $n = 1$ state in equation (7), what would be the radius of its magnified orbit?

As a multiple of the proton's effective radius, the distance of the $n = 1$ Bohr orbit is $a_0/10^{-15}$ m $\sim (5.29 \times 10^{-11}$ m)/ 10^{-15} m $\sim 52,900$. If the proton is expanded to a radius of 1 mm, then the electron will be orbiting at about (1 mm)(52,900) ~ 52.9 meters. In other words, if the expanded proton is placed at the center of a football field, the electron's orbit will reach to just beyond the goal lines!

More importantly, Equation (7) leads to an expression for the wavelengths of photon emitted when electrons transit between possible orbits, and to a theoretically predicted value of the Rydberg constant. To arrive at the wavelength expression, imagine that the electron falls from an initial orbital radius r_i to some final orbital radius r_f , with $r_f < r_i$. According to Equation (4), $E_f < E_i$ (both E_f and E_i are negative); if the energy lost by the electron is presumed to appear as a photon in accordance with Planck's hypothesis, then

$$E_{\text{photon}} = E_i - E_f = \frac{e^2}{8\pi\epsilon_0} \left(\frac{1}{r_f} - \frac{1}{r_i} \right) = h\nu_{i \rightarrow f}. \quad (9)$$

This would correspond to a photon of wavelength $\lambda = c/\nu$ or

$$\frac{1}{\lambda_{i \rightarrow f}} = \frac{e^2}{8\pi\epsilon_0 hc} \left(\frac{1}{r_f} - \frac{1}{r_i} \right). \quad (10)$$

Substituting Equation (7) for the orbital radii gives

$$\frac{1}{\lambda_{n_i \rightarrow n_f}} = \frac{m_e e^4}{8 \epsilon_0^2 h^3 c} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad (n_f < n_i). \quad (11)$$

Now recall the Balmer-Rydberg expression for the visible-region hydrogen-line wavelengths, Equation (1.2.2):

$$\frac{1}{\lambda_n} = R_H \left(\frac{1}{4} - \frac{1}{n^2} \right). \quad (12)$$

Equations (11) and (12) are remarkably similar in form; indeed, they correspond precisely if we take $n_f = 2$ and if the Rydberg constant is given by

$$R_H = \frac{m_e e^4}{8 \epsilon_0^2 h^3 c}. \quad (13)$$

Substitution of the appropriate numerical values yields $R_H = 109,737 \text{ cm}^{-1}$, in close agreement with the experimental value of $109,678 \text{ cm}^{-1}$. The slight discrepancy (0.05%) can be accounted for by the motion of the electron and proton about their mutual center of mass (Problem 1–11). With this agreement it is clear that Equation (11) will produce the observed wavelengths of the Balmer lines when $n_f = 2$. According to the Bohr model, the Balmer series of hydrogen lines corresponds to electrons transiting to the $n = 2$ orbit from “higher” orbits.⁶

Equation (11) is quite general, and can be used to calculate the wavelengths of whole series of spectral lines for hydrogen. Inverting it gives the wavelengths directly:

$$\lambda_{n_i \rightarrow n_f} = \frac{8 \epsilon_0^2 h^3 c}{m_e e^4} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)^{-1} = 911.75 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)^{-1} \text{ \AA}, \quad (14)$$

where the numerical value of 911.75 \AA accounts for electron/proton center-of-mass motion.

⁶A website giving the energy levels of hydrogen and deuterium for states $n = 1$ to 200 for all allowed angular momentum states (see Chapter 6) is available through the National Institute of Standards and Technology at <http://physics.nist.gov/PhysRefData/HDEL>.

EXAMPLE 1.2

Compute the wavelength of the $7 \rightarrow 4$ transition for a hydrogen atom. What is the energy of the photon emitted in such a transition, in eV?

From Equation (14)

$$\begin{aligned} \lambda_{7 \rightarrow 2} &= 911.75 \left(\frac{1}{4^2} - \frac{1}{7^2} \right)^{-1} \text{ \AA} = 911.75 \left(\frac{1}{16} - \frac{1}{49} \right)^{-1} \text{ \AA} \\ &= 911.75 \left(\frac{33}{784} \right)^{-1} \text{ \AA} = 21,661 \text{ \AA} \end{aligned}$$

With this wavelength, $2.166 \times 10^{-6} \text{ m}$, such a photon would lie in the *infrared* part of the electromagnetic spectrum, far to the red of human visual response. The energy is

$$\begin{aligned} E &= \frac{hc}{\lambda} = \frac{(6.6261 \times 10^{-34} \text{ J} \cdot \text{sec})(2.9979 \times 10^8 \text{ m/s})}{2.1661 \times 10^{-6} \text{ m}} \\ &= 9.171 \times 10^{-20} \text{ J} \end{aligned}$$

With $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$, this corresponds to about 0.57 eV.

Table 1.1 lists hydrogen spectral wavelengths computed from this formula for a number of (n_i, n_f) pairs. A group of lines corresponding to the same n_f is known as a **series** of lines. Each such series is characterized by a **series limit** corresponding to

Table 1.1 Hydrogen Transition Wavelengths (Å)

Final state	Initial state						Series
	2	3	4	5	6	Infinity	
1	1215.7	1025.7	972.5	949.7	937.8	911.8	Lyman
2		6564.6	4862.7	4341.7	4102.9	3647.0	Balmer
3			18756.0	12821.5	10941.0	8205.8	Paschen
4				40522.2	26258.4	14588.2	Brackett
5					74597.7	22794.3	Pfund
6						32824.2	Humphreys

$n_i = \infty$; the spacing of the lines decreases toward the series limits. As mentioned earlier, the range of human vision runs from about 3500–7000 Å; only the Balmer series lies entirely within these limits. The series corresponding to $n_f = 3$ lies in the infrared region of the spectrum, and had been observed in 1908 by Freidrich Paschen [10] to occur at exactly the wavelengths calculated by the Bohr formula. After publication of Bohr's theory the series corresponding to $n_f = 1, 4,$ and 5 were discovered by Lyman (1914), Brackett (1922), and Pfund (1924) [11–13]. These discoveries lent immense credibility to Bohr's theory.

The energy of an electron in quantum state n in the Bohr model is given by combining Equations (4) and (7):

$$E_n = -\frac{m_e e^4}{8\varepsilon_0^2 h^2 n^2} = -\frac{13.606}{n^2} \text{ eV} \quad (n = 1, 2, 3, \dots), \quad (15)$$

where the factor of 13.606 eV, known as the Rydberg energy, accounts for the electron/proton center-of-mass motion and the values of the various constants to five significant figures. This is one of the most famous results of early quantum mechanics. It tells us that to ionize a hydrogen atom from its **ground state** ($n = 1$) requires an expenditure of 13.6 eV of energy, precisely the observed value.

Figure 1.5 shows an **energy-level diagram** for hydrogen based on the Bohr model. Energy is plotted increasing upwards on the vertical axis; the horizontal axis has no physical meaning and serves only to improve the readability of the figure. The arrows show a number of possible quantum jumps or *transitions*; their lengths are proportional to the frequencies of the corresponding emitted photons because $E = h\nu$. Electrons that are initially not bound to the atom (so-called free electrons with $E > 0$) can become so by releasing just enough energy to bring them into one of the stationary states; thus, there is a **continuum** of energy levels with $E > 0$.

An intriguing aspect of Bohr's model concerns the orbital angular momentum of the electron, usually designated L . Classically, a mass m in a circular orbit of radius r and speed v has angular momentum $L = mvr$. If we apply this to the electron in the Bohr model with the help of Equations (6) and (7),

$$L = m_e v r = m_e \left(\frac{e^2}{2\varepsilon_0 n h} \right) \left(\frac{\varepsilon_0 h^2}{\pi m_e e^2} \right) n^2 = \left(\frac{h}{2\pi} \right) n, \quad (n = 1, 2, 3, \dots). \quad (16)$$

the physical interpretation of the result is that the orbital angular momentum of the electron is quantized in units of $h/2\pi$. Planck's constant, which was originally introduced to explain thermal radiation, now appears as a fundamental unit of angular momentum. Many treatments of the Bohr model begin by assuming that angular

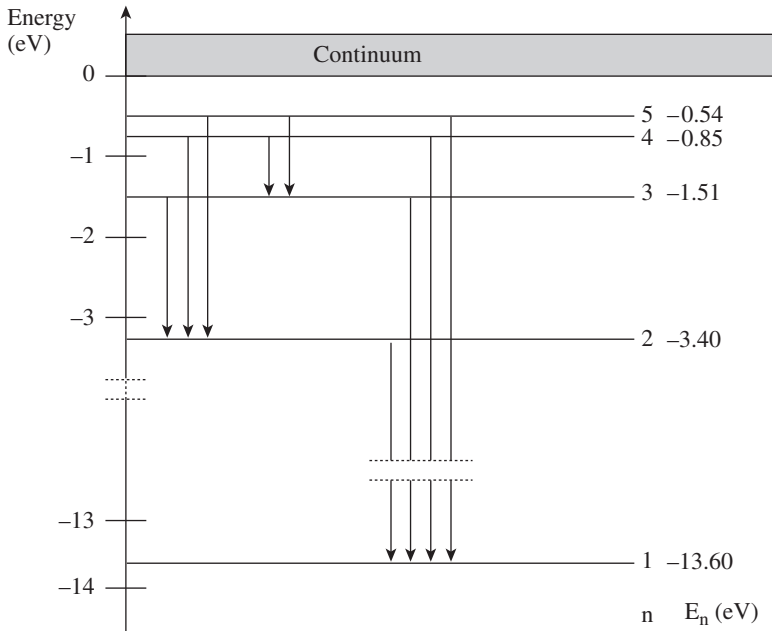


FIGURE 1.5 Energy Level Diagram for Hydrogen.

momentum is quantized in this way. Whether one regards E or L as being the fundamentally quantized attribute is arbitrary; the relationship is symbiotic. The fundamental quantum of angular momentum, $h/2\pi$, is given its own symbol, \hbar , read as “h-bar”:

$$\hbar = \frac{h}{2\pi} = 1.05459 \times 10^{-34} \text{ Joule-sec.} \quad (17)$$

We will see in Chapter 7 that angular momentum plays a central role in the wave mechanics of the hydrogen atom.

At this point, it is useful to look back at the illustration of Kirchoff’s laws, (Figure 1.1), and relate it to Bohr’s model. A cool gas will have most of its atoms in the lowest energy (ground) state. When light is passed through such a gas only those photons with energy equal to the various differences between the ground state and higher energy levels of the gas atoms will be absorbed out, causing certain wavelengths to be removed from the light beam. In the case of a hot gas, we will see photons emitted from de-excitations of the gas atoms: the reverse of the cool-gas excitation process. The continuous spectrum of a hot solid object (e.g., a lightbulb filament) is a manifestation of interactions between atoms.

EXAMPLE 1.3

One of the results of Planck's blackbody radiation theory is that any environment at absolute (Kelvin) temperature T will be teeming with photons of average energy $2.7kT$ where k is Boltzmann's constant. At room temperature (300 K), would this average energy be sufficient to ionize a hydrogen atom from the $n = 1$ state? If not, what temperature would result in such ionization?

The average photon energy evaluates as

$$\langle E \rangle = 2.7 (1.381 \times 10^{-23} \text{ J/K})T = 3.729 \times 10^{-23} T \text{ (Joules)}$$

if T is in Kelvins. This is equivalent to $2.327 \times 10^{-4}T$ eV. At $T = 300$ K, $\langle E \rangle = 0.07$ eV, far below the ionization energy of 13.6 eV. $\langle E \rangle = 13.6$ eV would require $T \sim 58,000$ K. In cosmology, the time after the Big Bang at which the Universe had cooled to this temperature is known as the *recombination time*—the point at which neutral hydrogen could form.

In the years following its publication, Bohr's theory underwent a number of refinements. Inclusion of elliptical orbits and relativistic effects led to some understanding of the "fine structure" of spectral lines. Experimental work by Henry Moseley [14] on X-rays, and by James Franck and Gustav Hertz [15] on collisions of electrons with atomic and molecular gases, added compelling evidence for the existence of quantized energy levels. Despite its success and powerful intuitive appeal, though, Bohr's model was not without problems. First was the sheer arbitrariness of the orbital frequencies assumption: It clearly works, but was there any way a more fundamental understanding might be sought? Despite years of effort by Bohr and his colleagues to extend the theory to more complex atoms, they had only very limited success [16]. Deeper understanding of these matters had to await a wave formulation of quantum mechanics in 1926.

EXAMPLE 1.4

X-rays are photons with wavelengths from 0.06 to 125 Å. In 1913–14, Henry Moseley provided supporting evidence for the Bohr model by measuring the wavelengths of photons emitted from (among others) $2 \rightarrow 1$ electronic transitions for metals of a variety of atomic numbers Z . To what range in Z does the X-ray part of the spectrum correspond for $2 \rightarrow 1$ transitions in the Bohr model?

From Equation (1.3.14) and the comment given regarding incorporating different Z values following Equation (1.3.1), we can write the Bohr transition wavelengths as

$$\lambda_{n_i \rightarrow n_f} = \frac{912}{Z^2} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)^{-1} \text{ \AA},$$

where we have rounded the Rydberg constant to the nearest Ångstrom. For $(n_i, n_f) = (2, 1)$ this becomes (again to the nearest Å)

$$\lambda_{2 \rightarrow 1} = \frac{1216}{Z^2} \text{ \AA}.$$

For $\lambda = 125 \text{ \AA}$ we find $Z \sim 142$, and for $\lambda = 0.06 \text{ \AA}$, $Z \sim 3$. Thus, essentially the whole of the periodic table was available to Moseley. Further details on Moseley's work appear in Section 1-10 of French and Taylor.⁷

■ 1.4 de Broglie Matter Waves

In his 1924 Ph.D. thesis, French physicist Louis de Broglie (pronounced “de broy”) proposed that if photons could behave like particles and transport momentum according to

$$p = \frac{h}{\lambda}, \tag{1}$$

then might material particles possessing momentum be accompanied by a **matter-wave** of wavelength given by inverting the relation: $\lambda = h/p = h/mv$?

The mathematical manipulation here is trivial, but the physical hypothesis seems absurd: We do not observe matter to be wavy; it is solid and localized. But just because we cannot see a particular phenomenon does not mean that it does not exist. The controlling factor in Equation (1) is the minuteness of Planck's constant. A mass of 1 kg moving at 1 meter/sec would have an associated **de Broglie wavelength** of $\sim 10^{-34}$ meters, some 20 orders of magnitude smaller than an atomic nucleus. We could scarcely hope to observe the “matter-wave” associated with such a macroscopic object. On the other hand, if an extremely tiny mass is involved, such as that of an electron, then it turns out that the associated wave can be comparable in size to its parent particle.

⁷Footnote to come?

Table 1.2 de Broglie Wavelengths.

Situation	λ (A)	Comment
Electron, energy 1 eV	12.3	Molecular size
Proton, energy 1 keV	0.009	Subatomic size
800 kg car @ 20 m/sec	4.1×10^{-28}	Nuclear size

Table 1.2 shows a few de Broglie wavelengths computed via the relationship now named after him [17]:

$$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2Km}}, \quad (v \ll c), \quad (2)$$

where K is the kinetic energy of the mass involved.

If particles really do possess associated waves, then it is clear that we can hope to detect them only in atomic-scale phenomena. Leaving aside for the moment the question of what they mean, let us ask how such matter-waves might manifest themselves.

Waves can be diffracted to produce constructive and destructive interference patterns. According to de Broglie, then, electrons fired through a double-slit apparatus should somehow interfere with each other (and themselves!). The problem is that the slit separation must be on the order of the wavelength involved, far too small (at least in de Broglie's day) to be physically manufactured. However, as de Broglie himself pointed out, nature provides natural diffraction gratings with spacings on the order of Ångstroms: the regularly spaced rows of atoms in metallic crystals. Less than three years after de Broglie advanced his hypothesis, experimental verification came independently from American and British groups of researchers. Working at the Bell Telephone Laboratories in the U.S., Clinton Davisson and Lester Germer observed, by accident, interference effects with electron scattering from crystals of nickel [18]. In Britain, George P. Thomson (J.J.'s son) verified the effect by scattering electrons through thin metallic foils [19]. In 1961, Claus Jonsson [20] demonstrated electron diffraction with a true double-slit arrangement, utilizing an elaborate array of electrostatic lenses to magnify the image. More recently, the wave properties of Carbon-60 "buckyball" molecules have been observed by similarly passing them through a series of slits,⁸ as has the diffraction of electrons by a standing light wave.⁹ All these experiments and many others have demonstrated that electrons, atoms, and molecules

⁸Physics Today 1992; 52(12):9

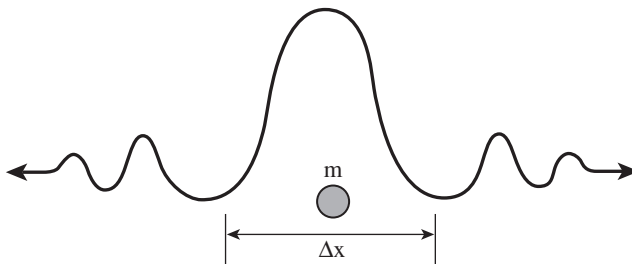
⁹Physics Today 2002; 55(1):15

behave in full agreement with de Broglie's hypothesis. The wave nature of electrons is put to stunning practical use in electron microscopy. The resolution of a microscope (the smallest distance by which two objects can be separated and still viewed as distinct) is proportional to the wavelength of light used. Because electrons behave as waves of wavelengths much shorter than that of visible light, much greater detail is resolvable. Images of individual molecules and atoms can be obtained in this way.

The evidence for de Broglie's matter-waves is incontrovertible. But what does it mean to say that a particle has a wave nature? How do we reconcile the classical point-mass view of matter with wave properties? As a schematic model, consider Figure 1.6.

The victim in this game of wavy particles is the classical idea that the position of the particle can be specified with an arbitrary degree of precision. In effect (but not in reality) the electron acts as if it is smeared out into a so-called wave packet that pervades all space. The amplitude of this wave, however, is not constant: it proves to be strongly peaked in the vicinity of the electron over a length scale Δx on the order of the size of the electron, as the figure suggests. For practical purposes, we can no longer specify with precision where the electron is; we can only speak meaningfully in terms of the *probability* of finding the electron at some position. (We will explore these "probability waves" further in subsequent chapters). It is this wavy nature of matter that lies at the heart of the Heisenberg uncertainty principle, which we will examine in Chapter 4.

These considerations in no way invalidate the application of Newtonian dynamics to objects such as golf balls or planets. The de Broglie waves accompanying such masses are so infinitesimally small in comparison with their length-scales that we cannot hope to detect them. Only when the size of the system under study is comparable to $\lambda = h/mv$ will quantum effects become noticeable. As an example, refer to Table 1.2. A 1 keV proton incident on a hydrogen atom has a de Broglie wavelength much less than the size of the atom; for practical purposes,



I FIGURE 1.6 A Particle and Its de Broglie Matter-Wave.

this will be a particle interaction. On the other hand, an electron of energy 1 eV has a de Broglie wavelength on the order of the size of that same hydrogen atom: to an imaginary observer riding on the atom the incoming electron would appear amorphous.

The “wave-particle duality” is perhaps the most counterintuitive aspect of quantum mechanics, and, not surprisingly, has inspired an extensive body of literature. An excellent discussion on this topic appears in the first two chapters of the third volume of Feynman’s *Lectures on Physics* [21]. A very readable and humorous look at the situation appears in “Two lectures on wave-particle duality” by Mermin.¹⁰

EXAMPLE 1.5

What speed must an electron have if its de Broglie wavelength is 5000 Å? A photon of this wavelength would be in the visible part of the electromagnetic spectrum.

Putting $p = mv$ in Equation (1) above and solving for v gives $v = h/m\lambda$, hence

$$v = \frac{h}{m\lambda} = \frac{(6.626 \times 10^{-34} \text{J} \cdot \text{s})}{(9.109 \times 10^{-31} \text{kg})(5 \times 10^{-7} \text{m})} = 1455 \text{ m/s.}$$

See Problem 1-20. If this speed were due to the electron’s random thermal motion in an environment at absolute temperature T , the environment would be at $T \sim 0.04 \text{ K}$. Electrons of such speed are thus characterized as “cold.”

EXAMPLE 1.6

De Broglie further hypothesized that the allowed orbits for an electron in a hydrogen atom are given by the condition that an integral number “ n ” de Broglie wavelengths fit around the circumference of the orbit. Show that this condition leads to the Bohr quantization condition on angular momentum, Equation (1.3.16).

Let the electron have speed v in an orbit of radius r . The circumference of the orbit is then $2\pi r$. de Broglie’s hypothesis is then that an integral number of wavelengths fit into this circumference:

$$\frac{2\pi r}{\lambda} = n.$$

¹⁰Mermin ND, *Physics Today* 1993; 46(1):9–11.

Setting $\lambda = h/m_e v$ gives

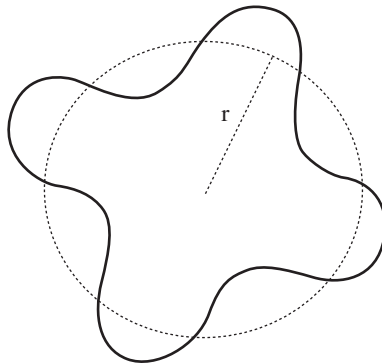
$$\frac{2\pi m_e v r}{h} = n.$$

However, $m_e v r$ is just the angular momentum of the electron in its orbit:

$$L = \left(\frac{h}{2\pi}\right)n = \hbar n,$$

precisely the Bohr quantization condition on L . If the condition on the electron's speed that emerged from Bohr's orbital frequency assumption is used here (Equation 1.3.6), the result is the same restriction on orbital radii and energies that emerged from his approach.

Figure 1.7 shows a sketch of what de Broglie had in mind: an integral number of wavelengths (in this case shown, $n = 4$) fitting around the circumference of an orbit like a standing wave. It should be emphasized that the amplitude of the wave shown in the sketch is purely arbitrary, de Broglie's relation gives no information on this.



I FIGURE 1.7 de Broglie's Quantization Condition.

■ Summary

The need to introduce the hypothesis that some physical quantities (such as energy and angular momentum) are quantized grew out of the inability of classical physics to provide adequate understanding of phenomena such as thermal radiation, atomic spectra, and atomic structure. The way was led by Max Planck, who in 1900 proposed that one could model the mechanism of thermal radiation by assuming that the source of black-body radiation lay in “oscillators” restricted to possessing energies given by

$$E = nh\nu,$$

where n is an integer ($n = 1, 2, 3, \dots$), h is Planck’s constant, and ν is the frequency of vibration. Later, Niels Bohr used this assumption in conjunction with a semiclassical planetary electron model of the hydrogen atom. The essence of Bohr’s model is that the orbiting electron is restricted to certain “stationary” energy states wherein it does not radiate. Atomic spectra are then presumed to be due to electrons executing transitions between different stationary states the difference in energy ΔE between the states appearing as a photon of energy $\Delta E = h\nu$ in accordance with Planck’s hypothesis. The energy level of a Bohr atom in quantum state n ($n = 1, 2, 3, \dots$) is given by

$$E_n = -\frac{m_e Z^2 e^4}{8\epsilon_0^2 h^2 n^2} = -13.595 \frac{Z^2}{n^2} \text{ eV} \quad (n = 1, 2, 3, \dots)$$

where Z is the number of protons in the nucleus. The wavelength of the photon emitted by an electron transiting from Bohr orbit n_i to orbit n_f ($n_i > n_f$) is given by

$$\lambda_{n_i \rightarrow n_f} = \frac{911.75}{Z^2} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)^{-1} \text{ \AA}.$$

A corollary of the Bohr model is that the orbital angular momentum of the electron is quantized in units of $h/2\pi$.

A central concept of the quantum aspect of nature is that of matter-waves, due to de Broglie. On the scale of atomic phenomena we are forced to abandon the notion of point particles in favor of treating them as being smeared out over a characteristic de Broglie wavelength given by

$$\lambda = \frac{h}{mv}.$$

The idea of matter-waves proves to be intimately related to the probability distribution interpretation of quantum mechanics.

■ Problems

- 1-1(E)** The table gives densities and atomic weights for a number of common elements.

Use Equation (1.1.1) to calculate approximate sizes for these species.

Element	Density (g/cm ³)	A (g/mol)
Al	2.7	27
Fe	7.88	56
Cu	8.96	64
Pb	11.34	207
Pt	21.45	195

- 1-2(E)** Consider a gas of “classical” Maxwell-Boltzmann atoms whose energies are distributed in accordance with Equation (1.2.5). In an environment of $T = 6000$ K (the approximate temperature of the surface of the Sun), what is the ratio of the number of atoms with energies between $E + dE$ to those with energies between $2E$ and $2E + dE$, where $E = 5$ eV?

- 1-3(I)** Equation (1.2.13) gives the amount of radiant energy $E_\nu d\nu$ between frequencies ν and $\nu + d\nu$ within a blackbody cavity. According to Einstein, the energy of an individual photon of frequency ν is $E = h\nu$. If the radiant energy is presumed to be comprised of individual photons, then the number of photons with frequencies between ν and $\nu + d\nu$ in the cavity would be given by $n_\nu d\nu = E_\nu d\nu / h\nu$. The total number of photons within the cavity will then be given by the integral of this expression for $\nu = 0$ to ∞ . Given that

$$\int_0^{\infty} \frac{x^2 dx}{(e^x - 1)} \sim 240,$$

determine the density of photons in a blackbody cavity at $T = 300$ K, about room temperature. Intergalactic space has a temperature of about 2.7 K; what is the density of photons in that environment?

- 1-4(E)** To establish the relationship between Equation (1.2.13) and Figure 1.3 requires some knowledge of thermodynamics, which shows that the rate of energy escape (power) between wavelengths λ and $\lambda + d\lambda$ through a hole of area A in a blackbody cavity of temperature T is given by

$$P(\lambda)d\lambda = A \left\{ \frac{2\pi hc^2}{\lambda^5 (e^{hc/\lambda kt} - 1)} \right\} d\lambda.$$

Consider a blackbody at $T = 7000$ K. What is the power emitted through a hole of area 1 m^2 between $\lambda = 4000 \text{ \AA}$ and 4001 \AA ? Does your result accord with Figure 1.3?

- 1-5(E)** Derive an expression for the speed of an electron in Bohr orbit n in terms of the speed of light. Is it justifiable to neglect relativistic effects in the development of the Bohr model?
- 1-6(E)** Repeat the derivation of the Bohr model for a lone electron orbiting a nucleus of Z protons. Use your results to compute ionization energies for a single electron orbiting nuclei of (a) helium, (b) carbon, and (c) uranium.
- 1-7(E)** Derive an expression for the centripetal force experienced by the electron in Bohr orbit n as a function of n and physical constants. What is the value of the force when $n = 1$? Modern force-probe microscopes are capable of measuring nano-Newton scale forces.
- 1-8(E)** An electron transits between two energy levels separated by energy E , emitting a photon of wavelength λ in accordance with the Planck/Bohr relation $E = hc/\lambda$.
- Show that if λ is given in units of Ångstroms, then $E = 12,398/\lambda$ electron-volts.
 - As a consequence of some perturbing effect, the separation of the energy levels is altered by an amount dE electron-volts. Show that the corresponding change in the wavelength of the emitted photon is $d\lambda = -\lambda^2 de/12,398$ Ångstroms. If a transition leading to a photon of wavelength 4000 \AA is perturbed by $dE = 0.01 \text{ eV}$, what is $d\lambda$?
- 1-9(I)** The purpose of this question is to derive an educated guess at the classically expected “lifetime” of an electron in various Bohr orbits. According to classical electrodynamics, an accelerated charge radiates energy at the rate $P = e^2 a^2 / 6\pi\epsilon_0 c^3$ Joule/sec, where a is the acceleration (v^2/r for a circular orbit). Decay rate (DR; unit = sec^{-1}) can be defined to be the power radiated divided by the energy emitted during the decay. Use

the Bohr model to derive an expression for DR for a decay from orbit n to orbit $n - 1$; for simplicity, use the acceleration for orbit n in the expression for P . The lifetime is given by the reciprocal of the decay rate; evaluate this numerically for $n = 2$.

- 1-10(E)** Both Newton's gravitational law and Coulomb's law are inverse-square laws: The force of attraction between the Sun (S) and the Earth (E) has magnitude $Gm_S m_E / r^2$, whereas the force of attraction between an electron and a proton in a hydrogen atom is $e^2 / 4\pi\epsilon_0 r^2$. Derive an expression for the equivalent of the Bohr radius for the gravitational case. What is the value of the quantum number of Earth's orbit? Would distance differences between individual quantum states in the solar system be observable?
- 1-11(A)** The text indicates how one can take into account the motions of the proton and electron around their mutual center of mass in the Bohr model. Using the condition that the center of mass of an isolated system must stay in the same place, derive the correction specified in the footnote, and hence derive the factor of 911.75 Å in Equation (1.3.14). *Hint:* Do not forget the kinetic energy of the proton about the electron/proton center of mass.
- 1-12(I)** It is remarked in the text that the effect of the motions of the electron and proton around their common center of mass in the Bohr model can be accounted for by substituting the reduced mass of the system, $m_e m_p / (m_e + m_p)$ in place of the electron mass m_e wherever the latter appears. An atom of deuterium consists of a lone electron orbiting a nucleus consisting of a proton and a neutron fused together; such a nucleus has mass close to $2m_p$. Show that the difference in wavelength between the Balmer $3 \rightarrow 2$ transition for deuterium versus ordinary hydrogen is given by

$$(\lambda_h - \lambda_d)_{3 \rightarrow 2} \sim \frac{144}{5} \frac{\epsilon_0^2 h^3 c}{m_p e^4}.$$

Evaluate this result numerically. If you have available a spectrometer capable of resolving spectral lines that are separated by no less than 2 Å, would you see the deuterium and hydrogen lines as separate?

- 1-13(E)** Write a computer program to compute the wavelengths of photons emitted by a single electron orbiting a hydrogen-like atom of nuclear charge $+Ze$ as it transits between any pair of states (n_i, n_f) (see Problem 1-6). Test your program by comparing your results with Table 1.1 for $Z = 1$. What are the wavelengths of the "Balmer series" for helium? For uranium?

1-14(I) Derive expressions for the lowest- and highest-possible wavelength photons emitted during transitions corresponding to a given series of spectral lines. Show that as a result, only the Lyman and Balmer series in hydrogen are not overlapped by lines from other series.

1-15(E) The *Ritz combination principle* was an empirical result that predated the Bohr model. This principle states that the inverse of the wavelength of a spectral line of some atomic species can often be predicted by computing the difference in the inverse wavelengths of two other spectral lines of the same species. Show that in the context of the Bohr model, hydrogen $p \rightarrow m$ transitions can be predicted from the $p \rightarrow n$ and $m \rightarrow n$ transitions according as

$$\frac{1}{\lambda_{p \rightarrow m}} = \frac{1}{\lambda_{p \rightarrow n}} - \frac{1}{\lambda_{m \rightarrow n}}.$$

Verify numerically by computing the $5 \rightarrow 3$ transition on the basis of the values for the $5 \rightarrow 1$ and $3 \rightarrow 1$ wavelengths given in Table 1.1.

1-16(I) A diatomic molecule (such as H_2) can be modeled as two point particles, each of mass m , joined by a rigid rod of length L . Assuming that the molecule rotates about an axis perpendicular to the rod through its midpoint and with angular momentum given by the Bohr condition (equation 1.3.16), derive an expression for the quantized values of the rotational energy.

1-17(I) As another model of an atom, consider a solid sphere of mass M and radius R rotating about an axis through its center in accordance with the Bohr quantization condition on angular momentum. Show that the possible rotational energies are given by $E_n = 5n^2h^2/16\pi^2MR^2$, where n is the quantum number. From this result derive an expression for the wavelength of a photon emitted as this system undergoes a transition from state $n + 1$ to state n . Evaluate your answer numerically for the case of M equal to the mass of a proton (essentially the mass of a hydrogen atom), $R = 1 \text{ \AA}$, and $n = 2$. Approximately what value would n have to be to give wavelengths in the optical region of the spectrum, $\lambda \sim 5000 \text{ \AA}$?

1-18(E) Compute the de Broglie wavelength for an electron of energy 1 keV. If this electron were interacting with a hydrogen atom, would classical mechanics suffice?

1-19(E) Particles in motion have associated de Broglie wavelengths. As a rule, if one is within a few de Broglie wavelengths of a particle, then the particle loses

its identity as a particle and acts more like a wave. The result is that classical mechanics no longer suffices to describe collisions. Rutherford investigated the scattering of α -particles (helium nuclei) from stationary gold nuclei, using classical mechanics to analyze the collisions. This question investigates the issue from a wave-mechanics perspective.

- a. Determine the de Broglie wavelength of an α -particle of kinetic energy 6 million electron-volts.
- b. The electrical potential energy of charges Q_1 and Q_2 separated by distance r is given by $U = Q_1Q_2/4\pi\epsilon_0r$. By equating the initial kinetic energy of the α -particle to the electrical potential energy, find the distance of closest approach of the α -particle to the gold nucleus, and so render a judgment as to how well-justified Rutherford was in his use of classical mechanics.

1-20(E) In kinetic theory, atoms are modeled as point masses of mass m , and the mean speed v of an atom in an environment at absolute temperature T is given by $mv^2 = 3kT$, where k is Boltzmann's constant. Derive an expression for the de Broglie wavelength for an atom of mass m at absolute temperature T in terms of h , k , T , and m . At room temperature, hydrogen atoms typically travel many thousands of Ångstroms between collisions; is it fair to treat them as effectively acting as point masses under such circumstances?

1-21(E) In a paper published in the October 14, 1999 edition of *Nature*,¹¹ a group at Universität Wien in Austria reported experimental detection of the de Broglie wave interference of Carbon-60 "buckyball" molecules. Such molecules consist of 60 carbon atoms arranged in a roughly spherical shape reminiscent of a soccer ball. In this experiment, the C-60 molecules had a most probable velocity of 220 m/s. Their data is well-fit by a de Broglie wavelength of 2.5 picometers. Verify this wavelength from the information given.

1-22(E) An atom of mass m is initially at rest with respect to an outside observer and has an electron in an excited state. The electron transits to a lower energy level, emitting a single photon of wavelength λ in the process. The emitted photon will have momentum $p = h/\lambda$. To conserve momentum, the atom must recoil with some speed v . Derive an expression giving the ratio of the

¹¹*Nature* 1999; 401:680–682

photon's energy to the kinetic energy of the recoiling atom in terms of λ , m , c , and h . A classical analysis will suffice for the recoiling atom. Evaluate the ratio numerically for a hydrogen atom emitting a photon of wavelength 5000 \AA . Based on your result, do you think it was reasonable to neglect the energy involved with the recoiling atom in the derivation of the Bohr model? Along these lines, the momentum transferred to an atom upon its absorbing a photon has actually been measured.¹²

¹²*Physics Today* 2005; 58(7):9