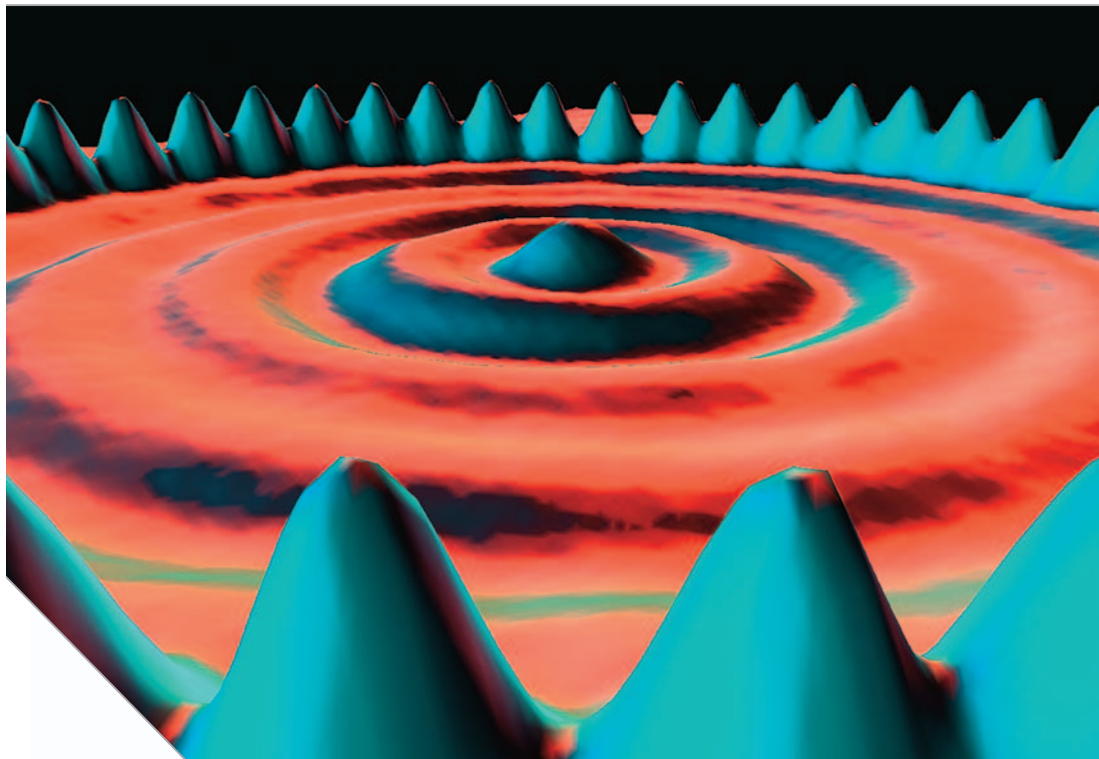# 1 Chapter

The Quantum Theory of the Submicroscopic World

Early attempts by nineteenth-century physicists to understand atoms and molecules met with only limited success. By assuming that molecules behave like rebounding balls, physicists were able to predict and explain some familiar phenomena, such as the pressure exerted by a gas. However, this model could not account for a number of newly discovered phenomena, such as the photoelectric effect or the emission spectra of atoms. The early twentieth century brought the development of quantum mechanics and the realization that the behavior of atoms and molecules cannot be described by the physical laws that work so well for everyday objects.

1.1 │ Classical Physics Does Not Adequately Describe the Interaction of Light with Matter

The motion of objects in the everyday world can be well described by the laws of *classical physics*—a description of the physical world that began with the development of the laws of motion by Isaac Newton. These laws were enormously successful as a unifying principle in physics until the end of the nineteenth century.

Science at the End of the Nineteenth Century: The Classical Model

The principal assumptions of classical physics can be summarized as follows:

1. The physical state of any system can be described by a set of quantities called *dynamical variables* that take on well-defined values at any instant of time.

2. The future state of any system is completely determined if the initial state of the system is known.

3. The energy of a system can be varied in a continuous manner over the allowed range.

If these assumptions seem quite reasonable, even obvious, to us, it is because they are consistent with our observations of the world in which we live. Up until 1900, the classical model was successful in describing accurately the motion of known objects up to the planetary scale, so it was widely assumed that this success would extend to the newly discovered submicroscopic world of atoms and molecules. However, as we will see, the classical model was unable to account for a number of experimental results that probed the nature of atoms and molecules and their interaction with light. This led to the discovery of *quantum mechanics,*[1] which represented a fundamental change in our understanding of the way nature works at the atomic scale.

Classical physics just before 1900 consisted of two major theoretical frameworks. The first was *classical mechanics,* which seeks to explain the motion of matter, and the second was the *wave theory of light,* a description of electromagnetic radiation.

Classical Mechanics

Classical mechanics as a unifying principle of physics began with Newton's laws of motion. As discussed in Section 0.1, Newton's second law

$$F = ma \tag{1.1}$$

relates the force (F) on an object to the product of its mass, m, and its acceleration[2] (a). Using Equation 1.1, the motion of an object can be determined if the initial velocity, $u_0 = u(t = 0)$, and initial position, $x_0 = x(t = 0)$, are known.

Consider, for example, the motion of a cannonball of mass m being fired through the air and subject to the gravitational pull of Earth. The variables that describe the

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1. Quantum mechanics was one of two major discoveries that revolutionized the world of physics at the beginning of the twentieth century. The other was the *theory of relativity,* developed by Albert Einstein, which changed the way scientists viewed the behavior of objects that were extremely fast or extremely massive. Unlike quantum mechanics, relativity was consistent with classical physics. Trying to reconcile the theory of relativity with that of quantum mechanics remains a major scientific challenge today.

2. In this and subsequent chapters, boldface type is used to indicate vector quantities, such as force (F) and acceleration (a).
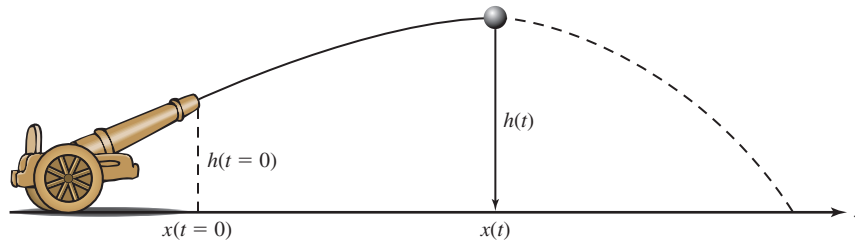
Figure 1.1 The trajectory of a cannonball in terms of the height *h* and the forward displacement *x*.

motion of the cannonball are the position and velocity (or momentum) of its center of mass. Using Newton's second law of motion (Equation 1.1), the precise trajectory of the ball (neglecting air friction) can be calculated if you know the initial position and initial velocity (momentum) of the ball. The position of the cannonball is defined by specifying the height above the ground *h* and the forward displacement *x* (see Figure 1.1), both of which are functions of the time *t*. The velocity of the ball is given by the corresponding vertical and horizontal velocity components, u_h and u_x. The gravitational force on the ball is given by *mg,* where *g* is the gravitational acceleration, which at the surface of Earth has the value $g = 9.80665$ m s^{-2}. For this system, Equation 1.1 can be solved as follows to give the trajectory of a cannonball, which is a parabola:

$$h(t) = h_0 + u_{h,0} t - \frac{1}{2} g t^2$$
$$x(t) = x_0 + u_{x,0} t$$

The velocities corresponding to $h(t)$ and $x(t)$ can also be determined:

$$u_h(t) = u_{h,0} - gt$$
$$u_x(t) = u_{x,0}$$

Thus, at any given time the position and velocity of the cannonball can be specified in terms of the initial values, consistent with the first two assumptions of classical physics. The energy of the cannonball is conserved in the motion and can be specified as the sum of the initial kinetic energy and the initial potential energy:

$$E = \left[\frac{1}{2} m u_{x,0}^2 + \frac{1}{2} m u_{h,0}^2 \right] + mgh_0$$

(The term in brackets is the total initial kinetic energy, which is the sum of the kinetic energies in the two directions of motion, *x* and *h.*) Because we can independently choose the initial position (by moving the cannon) and initial momentum (by controlling the amount of gunpowder used), the energy can be varied continuously over a wide range—a characteristic of classical theory.

Although a number of generalizations of Newton's laws of motion were developed in the eighteenth and nineteenth centuries, the basic framework of classical mechanics that they represent remained largely unchanged and unchallenged until 1900.

Wave Theory of Light
Parallel to the development of classical mechanics, the seventeenth through nineteenth centuries also saw tremendous progress in the understanding of light. In the seventeenth century, Isaac Newton performed the first quantitative study of the properties of light. He demonstrated that sunlight can be separated by a glass prism into a spectrum of distinct colors and that these colors can be recombined by directing this spectrum
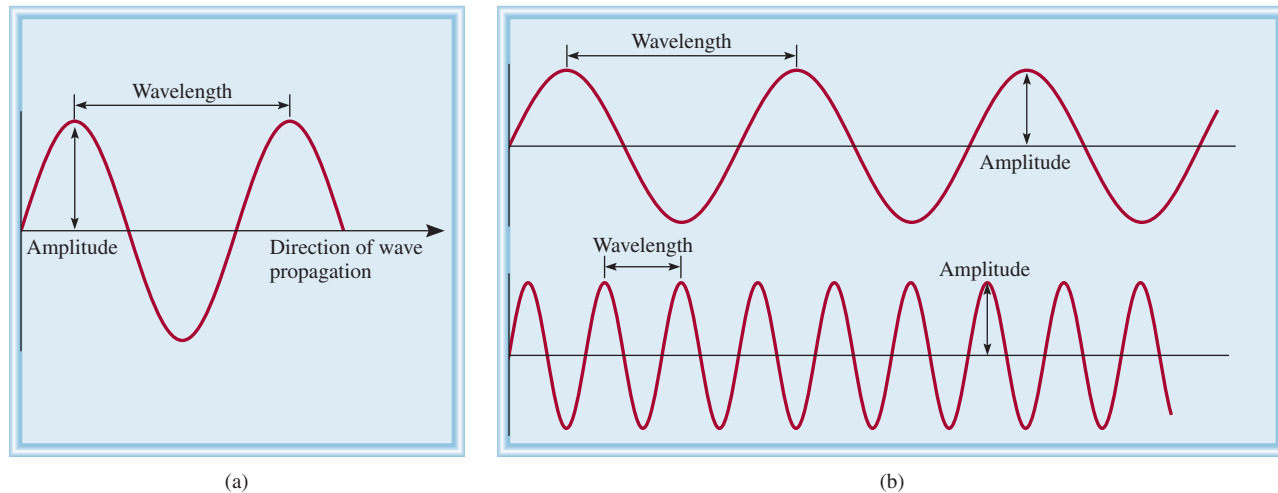
(a)   (b)

Figure 1.2 (a) Wavelength and amplitude. (b) Two waves having different wavelengths and frequencies. The wavelength of the top wave is three times that of the lower wave, but if both waves have the same speed, the frequency of the top wave is only one-third that of the lower wave. Both waves have the same amplitude.

through a second prism, turned opposite to the first, to reproduce white light. Although Newton explained much of this behavior by assuming that light was composed of discrete particles moving in straight lines, further work in the eighteenth and nineteenth centuries established light as a wave phenomenon.

Waves are characterized by their *wavelength*, *amplitude,* and *frequency* (Figure 1.2). The **wavelength** (λ) is *the distance between identical points on successive waves.* The **amplitude** of a wave is *the vertical distance from the midline of a wave to the peak or trough.* The **frequency** (ν) is the *number of waves that pass through a particular point in one second*. The speed of the wave (u) is the product of its wavelength and its frequency:

$$u = \lambda \nu \tag{1.2}$$

Wavelength is usually expressed in units of meters, centimeters, or nanometers, and frequency is measured in *hertz* (Hz) (after the German physicist Heinrich Rudolf Hertz[3]), where $1 \text{ Hz} = 1 \text{ s}^{-1}$.

When two (or more) waves interact, interference occurs. To understand this phenomenon, consider the interaction of two waves of equal wavelength, as shown in Figure 1.3. If the waves are *in phase,* that is, the positions the maximum and minimum of wave 1 match those of wave 2, as in Figure 1.3(a), then the two waves will add to give a wave that has twice the amplitude of the original two waves. This is called *constructive interference*. On the other hand, in Figure 1.3(e) the two waves are exactly out of phase, that is, the position of the minimum for wave 1 corresponds to the maximum of wave 2. When these two waves are added together, they exactly cancel one another to give zero. This is called *destructive interference*. If the waves are only partially out of phase, as in Figures 1.3(b)–(d), the waves

3. Heinrich Rudolf Hertz (1857–1894). German physicist. He performed a number of experiments confirming Maxwell's theory of electromagnetic radiation. His discovery of radio waves led to the development of the wireless telegraph and the radio.
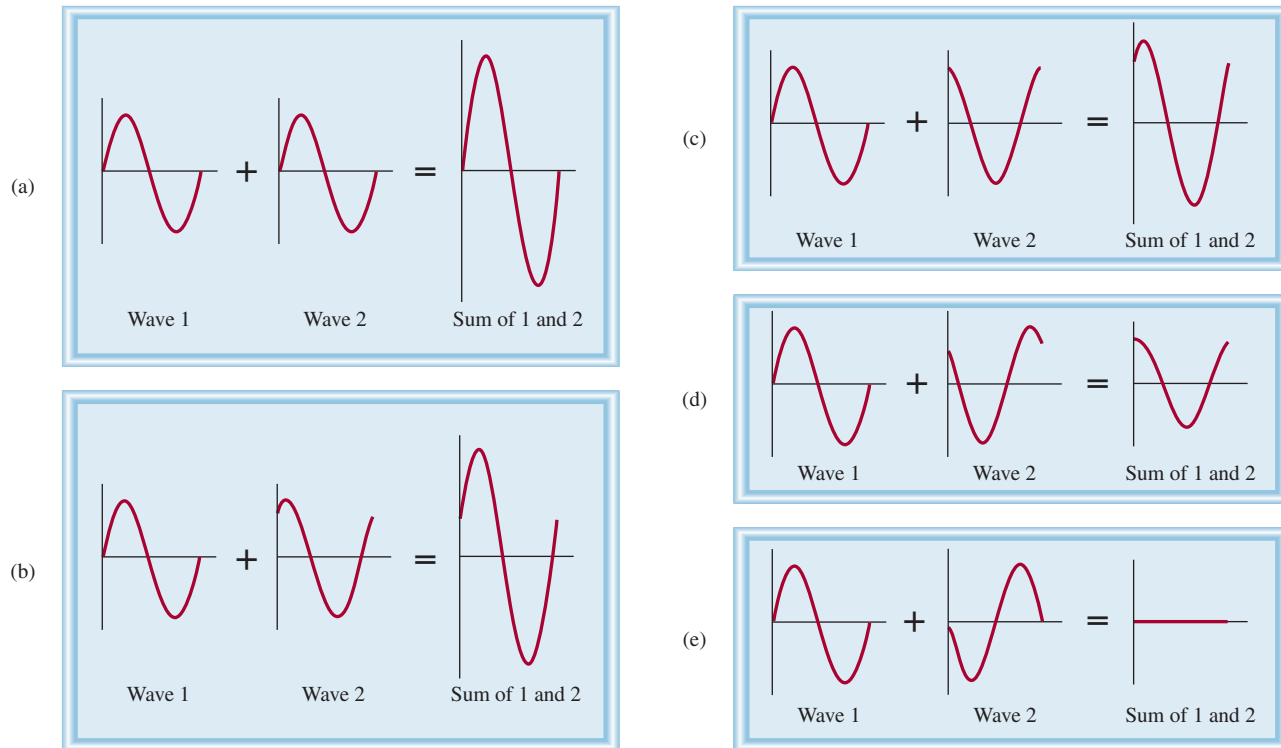
Figure 1.3 Constructive and destructive interference between two waves of equal wavelength and amplitude: (a) two waves completely in phase; (b)–(d) two waves partially out of phase; and (e) two waves exactly out of phase.

will add to give a wave with an amplitude that is intermediate between the two extremes in Figures 1.3(a) and (e). Experimentally, this phenomenon can be observed in a two-slit experiment, such as that shown in Figure 1.4. A light source emitting a single wavelength of light (called *monochromatic* light) is directed at a partition with two openings (slits A and B). These slits are small relative to the distance between them and act as two separate light sources. The two light waves emerging from slits A and B will interfere both constructively and destructively. The resulting interference patterns are observed on a screen as alternating bright and dark regions, respectively.
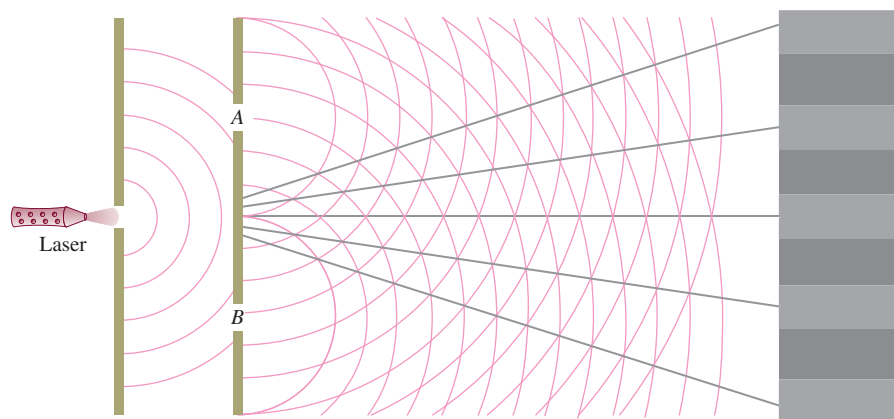

Figure 1.4 Two-slit experiment demonstrating the interference phenomenon. The pattern on the screen consists of alternating bright and dark bands.

Figure 1.5 Electric field component and magnetic field component of an electromagnetic wave. These two components have the same wavelength, frequency, and amplitude, but oscillate in two mutually perpendicular planes. The wave here is traveling along the *x* direction.
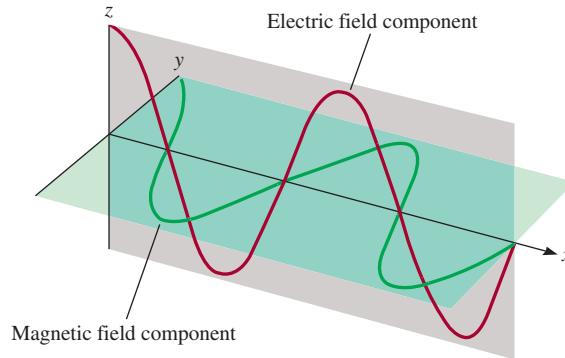
James Clerk Maxwell

A major breakthrough in understanding the wave nature of light came in the mid-nineteenth century when James Clerk Maxwell[4] developed the unified theory of the electromagnetic field. This theory, embodied by the Maxwell equations, predicted the existence of electromagnetic waves consisting of an electric-field component and a magnetic-field component oscillating in mutually perpendicular planes, both perpendicular to the direction of travel (see Figure 1.5). The calculated velocity of these waves matched precisely the known speed of light (*c*) in a vacuum (about 3.00×10^8 m s^{-1}), leading Maxwell to be the first to predict that light is just one form of electromagnetic radiation.

Maxwell's theory of electromagnetic radiation fits within the classical doctrine because the electric and magnetic fields (and their rates of change with time) take on well-defined values at all times and the future values of the fields can be predicted with arbitrary precision from their initial state using the Maxwell equations. In Maxwell's theory the energy of the electromagnetic wave depends upon the amplitude of the electromagnetic wave, but not on its frequency, and can be varied continuously.

Visible light was not the only type of radiation described as electromagnetic waves by Maxwell's theory. Figure 1.6 shows various types of electromagnetic radiation, which differ from one another in wavelength and frequency. Long radio waves are those emitted by large antennas, such as those used by broadcasting stations. The motions of electrons within atoms and molecules can produce shorter, visible light waves. The shortest waves, which also have the highest frequency, are associated with γ (or *gamma*)-rays, which result from changes within the nucleus of the atom. As we will discuss shortly, the higher the frequency, the more energetic the radiation, contrary to Maxwell's classical theory. Thus, ultraviolet radiation, X-rays, and γ-rays are high-energy radiation.

Example 1.1

The wavelength of the green light from a traffic signal is centered at 522 nm. What is the frequency of this radiation?

Strategy We are given the wavelength of an electromagnetic wave and asked to calculate its frequency (ν). Rearranging Equation 1.2 and replacing *u* with *c* (the speed of light) gives

$$\nu = \frac{c}{\lambda}$$

—Continued

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4. James Clerk Maxwell (1831–1879). Scottish physicist. Maxwell was one of the great theoretical physicists of the nineteenth century; his work covered many areas of physics, including the kinetic molecular theory of gases, thermodynamics, and electricity and magnetism.
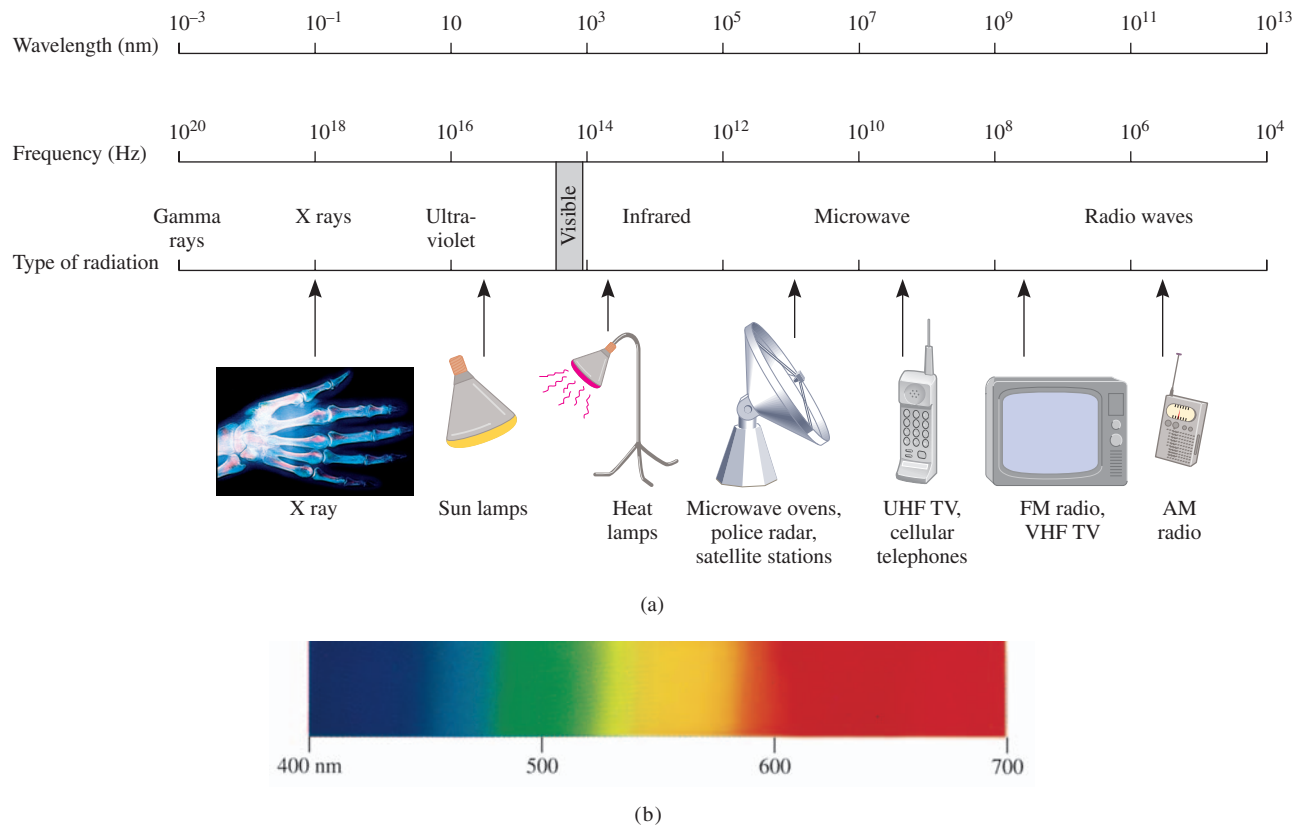
Figure 1.6 (a) Types of electromagnetic radiation. Gamma-rays have the shortest wavelength and highest frequency; radio waves have the longest wavelength and the lowest frequency. Each type of radiation is spread over a specific range of wavelengths (and frequencies). (b) Visible light ranges from a wavelength of 400 nm (violet) to 700 nm (red).

Continued—

Solution Because the speed of light is given in meters per second, it is convenient to first convert wavelength to meters. Recall that 1 nm $= 1 \times 10^{-9}$ m. We write

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m s}^{-1}}{522 \text{ nm}} \times \frac{1 \text{ nm}}{1 \times 10^{-9} \text{ m}} = 5.75 \times 10^{14} \text{ s}^{-1} = 5.75 \times 10^{14} \text{ Hz}$$

Practice Exercise The broadcast frequency of a certain radio station is 91.5 MHz. What is the wavelength of these radio waves?

Blackbody Radiation: The Failure of Classical Theory

Any object will radiate energy in the form of electromagnetic radiation purely as a consequence of its temperature. The red glow of an electric heater and the bright white light of the tungsten filament in an incandescent light bulb are familiar examples. This radiation is referred to as ***blackbody radiation***.[5] The physical properties

The red glow of an electric heater is an example of blackbody radiation.

5. A *blackbody* is an idealized object that absorbs 100 percent of the radiation that is incident upon it. No real object is a perfect blackbody.

Figure 1.7 The intensity of blackbody radiation as a function of wavelength at various temperatures.
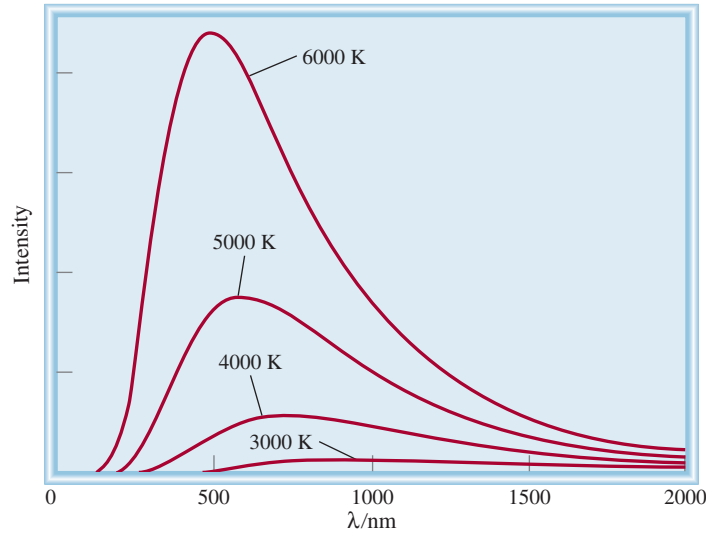
of blackbody radiation depend only on the temperature of the object, not on its composition.

If we measured the intensity of blackbody radiation versus the wavelength emitted at different temperatures, we would obtain a series of curves similar to the ones shown in Figure 1.7. Experiments at the end of the nineteenth century by Josef Stefan[6] and Wilhelm Wien[7] led to two important empirical laws of blackbody radiation, now named the Stefan-Boltzmann law and Wien's law. (An *empirical law* is one that is formulated purely on the basis of experimental data.)

▶ *Stefan-Boltzmann law:* The total intensity of blackbody radiation emitted by an object (obtained by integrating the curves in Figure 1.7 over all wavelengths) is proportional to the fourth power of the absolute temperature (that is, the temperature in kelvins, see Appendix 1):

$$\frac{\text{emitted power}}{\text{surface area of object}} = \sigma T^4$$

where $\sigma = 5.670 \times 10^{-8}$ W m^{-2} K^{-4} is the Stefan-Boltzmann constant and T is the absolute temperature. The law was used by Stefan to estimate the surface temperature of the sun. (Ludwig Boltzmann[8] is associated with this law because he was able to derive it using thermodynamic arguments five years after Stefan's experiments.)

▶ *Wien's law:* The wavelength of maximum intensity (λ_{max}) is inversely proportional to the absolute temperature:

$$T\lambda_{max} = \text{constant} = 1.44 \times 10^{-2} \text{ K m}$$

6. Josef Stefan (1835–1893). Austrian physicist. In addition to his quantitative experiments on blackbody radiation, he made important contributions to the kinetic theory of heat and to the theory of heat conduction in fluids.

7. Wilhelm Wien (1864–1928). German physicist. He received the Nobel Prize in Physics in 1911 for his work on blackbody radiation and also made important contributions to hydrodynamics and radiation theory.

8. Ludwig Boltzmann (1844–1906). Austrian physicist. Although Boltzmann was one of the greatest theoretical physicists of all time, his work was not recognized by other scientists in his lifetime. Suffering from poor health and great depression, he committed suicide in 1906.
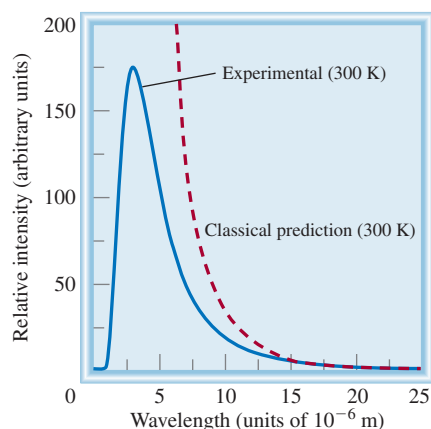
Figure 1.8 Experimental data (solid line) versus the classical prediction (dotted line) for the intensity as a function of frequency of the blackbody radiation from an object at a temperature of 300 K.

These experimental results caused a sensation among scientists at the time because they could not be explained using classical theory. The classical electromagnetic theory of light developed by Maxwell predicted that the energy of a light wave is a function only of the amplitude of the wave and does not depend on its wavelength (or frequency); therefore, the energy emitted by the object should be distributed equally among all possible electromagnetic waves without regard to frequency. However, for electromagnetic waves in three dimensions, there are many more oscillation modes of electromagnetic radiation possible at high frequency than exist at low frequency;[9] therefore, classical theory predicts that the intensity of blackbody radiation should increase with increasing frequency (decreasing wavelength). As a result, the classical model predicts that even objects at room temperature will emit high intensity ultraviolet, X-ray, and even γ-ray radiation—in effect, all objects in the universe should be infinitely bright! (This erroneous prediction is referred to as the *ultraviolet catastrophe.*) Comparing (Figure 1.8) the classical intensity with that observed experimentally for an object shows that the classical model works well at long wavelengths (low frequencies), but it drastically overestimates the intensity of high frequency electromagnetic waves in the blackbody radiation spectrum. Something fundamental was missing from the laws of classical physics!

Planck's Quantum Hypothesis

In 1900, Max Planck[10] solved the problem of blackbody radiation with an assumption that departed drastically from accepted concepts. Classical physics assumed that atoms and molecules could emit (or absorb) any arbitrary amount of radiant energy. Planck hypothesized that atoms and molecules could emit (or absorb) energy only in discrete quantities, like small packages or bundles. Planck gave the name **quantum** to *the smallest quantity of energy that can be emitted (or absorbed) in the form of electromagnetic radiation.* The energy E of a single quantum of electromagnetic energy is given by

$$E = h\nu \tag{1.3}$$

where h is called *Planck's constant* and ν is the frequency of the radiation. The value of Planck's constant has been determined experimentally to be 6.62608×10^{-34} J s.

9. For much the same reason that there are many more ways to write a large integer as the sum of two positive integers than there are ways to represent a smaller integer in the same manner.

10. Max Karl Ernest Ludwig Planck (1858–1947). German physicist. Planck received the Nobel Prize in Physics in 1918 for his quantum theory. He also made significant contributions in thermodynamics and other areas of physics.

Max Planck

According to quantum theory, the energy of electromagnetic radiation of frequency ν is always emitted in multiples of $h\nu$; for example, $h\nu$, $2h\nu$, $3h\nu$, . . . but never, for example, $1.67h\nu$ or $4.98h\nu$. At the time Planck presented his theory, he could not explain why energies should be fixed or quantized in this manner. Starting with this hypothesis, however, he had no trouble correlating the experimental data for the emission by solids over the *entire* range of wavelengths; they all supported the quantum theory.

The idea that energy should be quantized or "bundled" may seem strange, but the concept of quantization has many analogies. For example, an electric charge is quantized; there can be only whole-number multiples of e, the charge of one electron. Matter itself is quantized, because the numbers of electrons, protons, and neutrons and the numbers of atoms in a sample of matter must also be integers.

How does the Planck model explain the decrease in the intensity of blackbody radiation at high frequency (short wavelength)? At any given temperature, there is only a fixed average amount of thermal energy that is available to excite a given electromagnetic oscillation (light wave). In the classical model, where you can put an arbitrary amount of energy into any oscillation, the energy can be distributed evenly among the oscillations, regardless of frequency. In the Planck model, however, there is a minimum amount of energy that can be transferred into an electromagnetic oscillation from the object and this minimum energy (the quantum) increases with increasing frequency. For low-frequency electromagnetic waves, the quantum of energy is much smaller than the average amount of thermal energy available for the excitation of that electromagnetic wave; therefore, this energy can be evenly distributed among these oscillation modes, as in the classical model. For high frequencies, however, the quantum of energy is greater than the average available thermal energy and excitation into high frequency modes is inhibited.
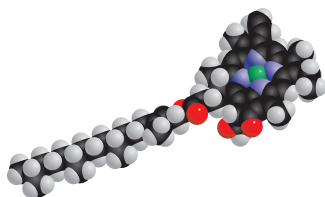
Example 1.2

Chlorophyll-a is green because it absorbs blue light at about 435 nm and red light at about 680 nm, so that mostly green light is transmitted. Calculate the energy per mole of photons at these wavelengths.

Strategy Planck's equation (Equation 1.3) gives the relationship between energy and *frequency* (ν). Because we are given wavelength (λ), we must use Equation 1.2, in which u is replaced with c (the speed of light), to convert wavelength to frequency. Finally, the problem asks for the energy per mole, so we must multiply the result we get from Equation 1.3 by Avogadro's number.

Solution The energy of one photon with a wavelength of 435 nm is

$$E = h\nu = h\left(\frac{c}{\lambda}\right) = (6.626 \times 10^{-34} \text{ J s})\frac{3.00 \times 10^8 \text{ m s}^{-1}}{435 \text{ nm } (1 \times 10^{-9} \text{ m nm}^{-1})}$$
$$= 4.57 \times 10^{-19} \text{ J}$$

For one mole of photons, we have

$$E = (4.57 \times 10^{-19} \text{ J})(6.022 \times 10^{23} \text{ mol}^{-1})$$
$$= 2.75 \times 10^5 \text{ J mol}^{-1}$$
$$= 275 \text{ kJ mol}^{-1}$$

Using an identical approach for the photons at 680 nm, we get $E = 176 \text{ kJ mol}^{-1}$.

Practice Exercise X-rays are convenient to study the structure of crystals because their wavelengths are comparable to the distances between near neighbor atoms (on the order of a few Ångstroms, where $1\text{Å} = 1 \times 10^{-10}$ m). Calculate the energy of a photon of X-ray radiation with a wavelength of 2.00 Å.

Chlorophyll-a

The Photoelectric Effect

In 1905, only five years after Planck presented his quantum theory, Albert Einstein[11] used the theory to explain the ***photoelectric effect***—a phenomenon in which *electrons are ejected from the surface of certain metals exposed to electromagnetic radiation* (Figure 1.9).

Experimentally, the photoelectric effect is characterized by three primary observations:

1. The number of electrons ejected is proportional to the intensity of the light.
2. No electrons can be ejected if the frequency of the light is lower than a certain *threshold frequency,* which depends upon the identity of the metal.
3. The kinetic energy of the ejected electrons is proportional to the difference between the frequency of the incident light and the threshold frequency.

The photoelectric effect could not be explained by the wave theory of light. In the wave theory the energy of a light wave is proportional to the square of the amplitude (intensity) of the light wave, not its frequency. This contradicts the second observation of the photoelectric effect. Building on Planck's hypothesis, Einstein was able to explain the photoelectric effect by assuming that light consisted of particles (light quanta) of energy $h\nu$, where ν is the frequency of the light. These particles of light are called ***photons.*** Electrons are held in a metal by attractive forces, and so removing them from the metal requires light of a sufficiently high frequency (which corresponds to a sufficiently high energy) to break them free. We can think of electromagnetic radiation (light) striking the metal as a collision between photons and electrons. According to the law of conservation of energy, we have energy input equal to energy output. If ν exceeds the threshold frequency, Einstein's theory predicts

$$h\nu = \Phi + \frac{1}{2}m_e u^2 \qquad (1.4)$$

where Φ (called the *work function*) is the energy needed to extract the electron from the metal surface and $\frac{1}{2}m_e u^2$ is the kinetic energy of the ejected electron. The work function measures how strongly the electrons are held in the metal. The threshold frequency is the smallest frequency for which Equation 1.4 has a solution. This occurs when the kinetic energy of the electron is zero, in which case Equation 1.4 gives

$$\nu_{\text{threshold}} = \frac{\Phi}{h}$$

Substituting this expression for $\nu_{\text{threshold}}$ into Equation 1.4 gives, after rearrangement,

$$\text{kinetic energy} = \frac{1}{2}m_e u^2 = h(\nu - \nu_{\text{threshold}})$$

Thus, Einstein's theory predicts that the kinetic energy of the ejected electron is proportional to the difference between the incident and threshold frequencies, as required.

---

11. Albert Einstein (1879–1955). German-born American physicist. Regarded by many as one of the two greatest physicists the world has known (the other is Isaac Newton). The three papers (on special relativity, Brownian motion, and the photoelectric effect) that he published in 1905 while employed as a technical assistant in the Swiss patent office in Berne have profoundly influenced the development of physics. He received the Nobel Prize in Physics in 1921 for his explanation of the photoelectric effect.
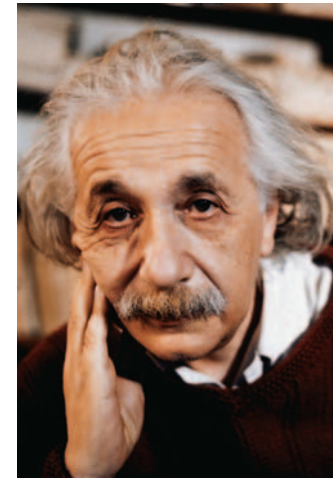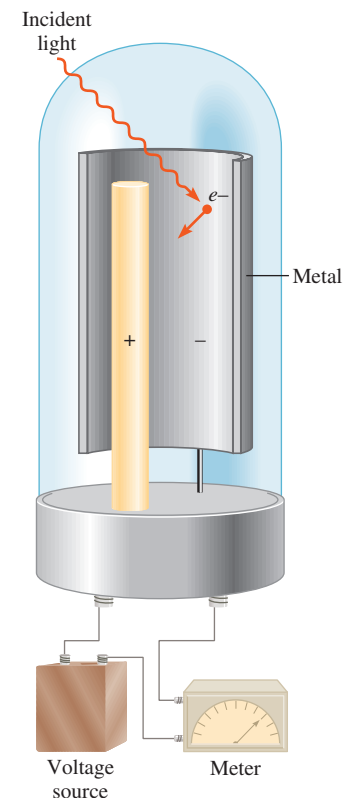
Albert Einstein

Figure 1.9 An apparatus for studying the photoelectric effect. Light of a certain frequency falls onto a clean metal surface and the ejected electrons are attracted toward the positive electrode. A detecting meter registers the flow of electrons.

Figure 1.10 A plot of the kinetic energy of ejected electrons versus the frequency of incident radiation.

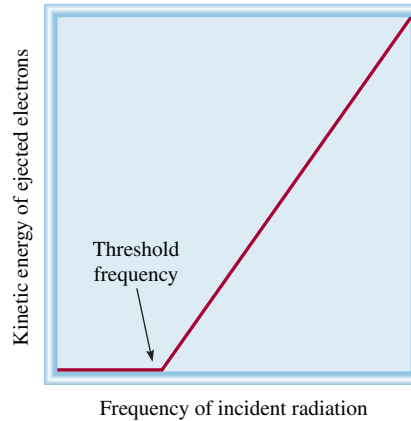

Frequency of incident radiation

Figure 1.10 shows a plot of the kinetic energy of ejected electrons versus the frequency of applied electromagnetic radiation.

Example 1.3

When 430-nm wavelength light is shined on a clean surface of sodium metal, electrons are ejected with a maximum kinetic energy of 0.83×10^{-19} J. Calculate the work function for sodium metal and the maximum wavelength of light that can be used to eject electrons from sodium.

Strategy We can use Equation 1.4 to find the work function if we know the excess kinetic energy and the frequency of the incident light. We are given the wavelength so we must use the speed of light (c) in place of u in Equation 1.2 to convert wavelength to frequency (remembering also to convert nanometers to meters). The maximum wavelength (minimum frequency) light that can be used to eject electrons is that which gives a zero electron kinetic energy—that is, all of the energy goes into ejecting the electron.

Solution From Equation 1.4

$$\Phi = h\nu - \text{(kinetic energy)}$$
$$= \frac{hc}{\lambda} - \text{(kinetic energy)}$$
$$= \frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^8 \text{ m s}^{-1})}{(430 \text{ nm})(10^{-9} \text{ m nm}^{-1})} - 8.3 \times 10^{-20} \text{ J}$$
$$= 3.8 \times 10^{-19} \text{ J}$$

To find the maximum wavelength, we combine Equation 1.2 with Equation 1.4 except we set the kinetic energy term on the right hand side of Equation 1.4 to zero, giving

$$h\nu_{\text{min}} = h\frac{c}{\lambda_{\text{max}}} = \Phi$$
$$\lambda_{\text{max}} = \frac{hc}{\Phi}$$
$$= \frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^8 \text{ m s}^{-1})}{3.8 \times 10^{-19} \text{ J}}$$
$$\lambda_{\text{max}} = 5.20 \times 10^{-7} \text{ m} = 520 \text{ nm}$$

Continued—

Practice Exercise   The work function for Al is 6.54×10^{-19} J. Calculate the wavelength of light (in nm) that will eject electrons with a maximum kinetic energy of 1.00×10^{-19} J and the maximum wavelength of light (in nm) that can be used to eject electrons from Al.

Einstein's theory posed a dilemma for scientists. On the one hand, it explained the photoelectric effect satisfactorily. On the other hand, the particle theory of light was inconsistent with the known wave behavior of light. The only way to resolve the dilemma was to accept the idea that light possesses *both* particlelike and wavelike properties. Depending on the experiment, light behaves either as a wave or as a stream of particles. This concept was totally alien to the way physicists had thought about radiation and its interaction with matter, and it took a long time for them to accept it. We will see in Section 1.3 that a dual nature (particles and waves) is not unique to light but is characteristic of all matter, including electrons.

1.2 | The Bohr Model Was an Early Attempt to Formulate a Quantum Theory of Matter

The work of Planck and Einstein showed that the energy of electromagnetic radiation at a given frequency (*v*) is quantized in units of *hv*. The extension of this quantum hypothesis to matter paved the way for the solution of yet another nineteenth-century mystery in physics: the emission spectra of atoms.

Emission Spectra of Atoms: Evidence of the Energy Quantization of Matter

Ever since the seventeenth century, chemists and physicists have studied the characteristics of **emission spectra,** which are *either continuous or line spectra of the radiation emitted by substances.* The emission spectrum of a substance can be seen by energizing a sample of material either with thermal energy (heating) or with some other form of energy (such as a high-voltage electrical discharge). A "red-hot" or "white-hot" iron bar freshly removed from a high-temperature source produces a characteristic glow. This visible glow is the portion of its emission spectrum that is sensed by eye. The warmth of the same iron bar represents the infrared region of its emission spectrum.

The emission spectra of the sun and of a heated solid are both continuous; that is, all wavelengths of visible light are represented in the spectra (see the visible region in Figure 1.6). The emission spectra of atoms in the gas phase, on the other hand, do not show a continuous spread of wavelengths from red to violet; rather, the atoms produce bright lines in different parts of the visible spectrum. These **line spectra** are *light emissions at specific wavelengths.* Figure 1.11 is a schematic diagram of a discharge tube that is used to study emission spectra, and Figure 1.12 shows the wavelengths of visible light emitted by a hydrogen atom. Every element has a unique emission spectrum.
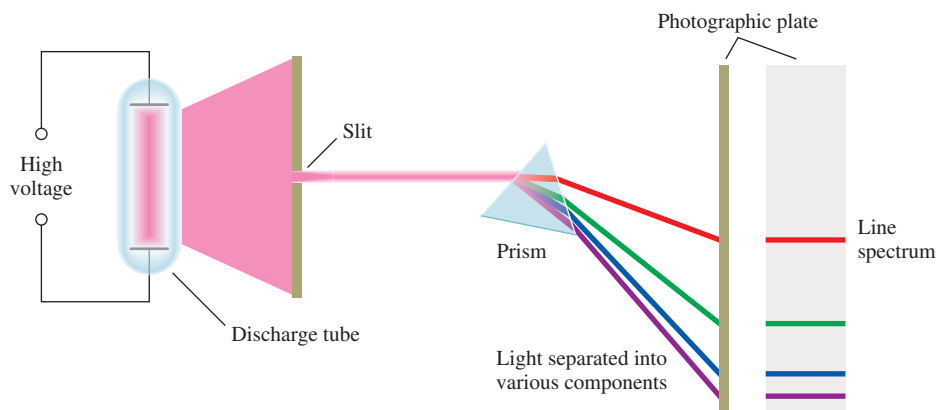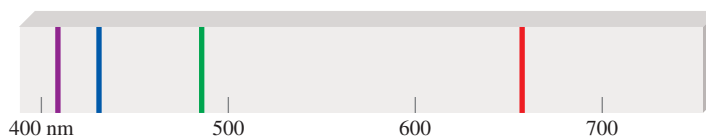
Figure 1.11 An experimental arrangement for studying the emission spectra of atoms and molecules. The gas under study is in a discharge tube containing two electrodes. As electrons flow from the negative electrode to the positive electrode, they collide with the gas. This collision process eventually leads to the emission of light by the atoms (or molecules). The emitted light is separated into its components by a prism. Each component color is focused at a definite position, according to its wavelength, and forms a colored image of the slit on the photographic plate. The colored images are called spectral lines.

Figure 1.12 The line emission spectrum of hydrogen atoms in the visible region.

The characteristic lines in atomic spectra can be used in chemical analysis to identify unknown atoms, much as fingerprints are used to identify people. When the lines of the emission spectrum of a known element exactly match the lines of the emission spectrum of an unknown sample, the identity of the sample is established. Although the utility of this procedure had long been recognized in chemical analysis, the origin of these lines was unknown until early in the twentieth century. Figure 1.13 shows the emission spectra of several elements.

The Emission Spectrum of Hydrogen

At the end of the nineteenth century, physicists began exploring the emission spectra of atoms in quantitative detail. Of particular interest, because of the simplicity and importance of the first element, was the emission spectrum of hydrogen (Figure 1.13). The Swedish physicist Johannes Rydberg[12] analyzed the existing experimental data and formulated the following equation for the frequencies of the lines in the hydrogen emission spectrum:

$$\nu = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \tag{1.5}$$

where n_1 and n_2 are positive integers with $n_2 > n_1$, and R_H is the ***Rydberg constant,*** which has the experimental value 3.290×10^{15} s^{-1}.

Color emitted by hydrogen atoms in a discharge tube. The color observed results from the combination of the colors emitted in the visible spectrum.

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12. Johannes Robert Rydberg (1854–1919). Swedish mathematician and physicist. Rydberg's major contribution to physics was his study of the line spectra of many elements.
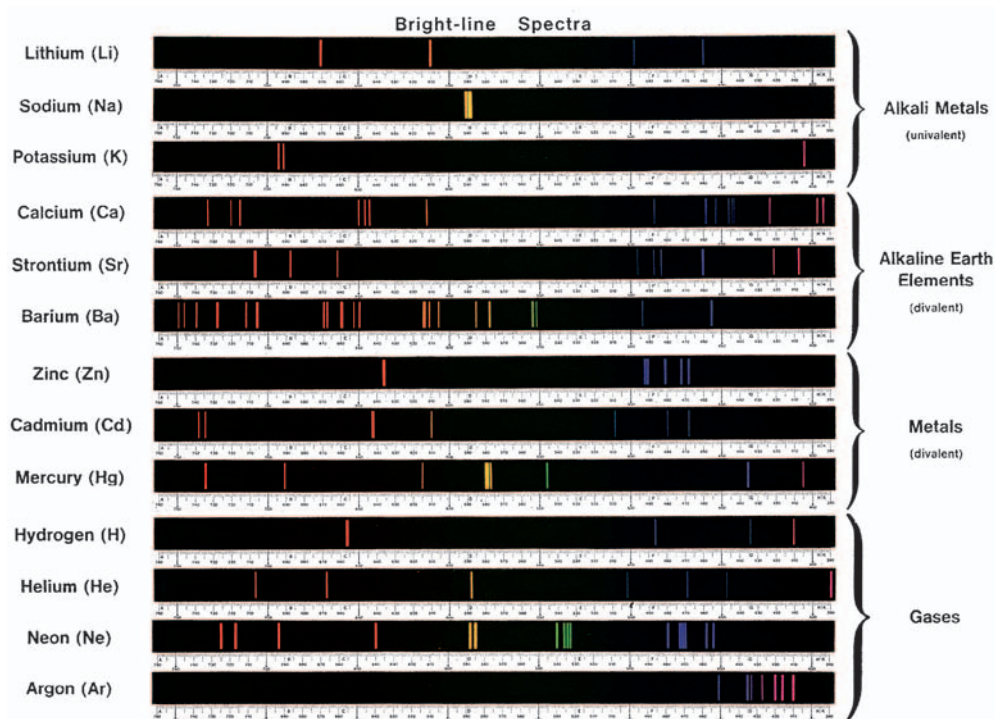
Figure 1.13 The emission spectra of various elements.

Equation 1.5 accurately predicts all of the known lines in the emission spectrum of hydrogen. The emission lines are often classified in terms of the value of n_1. Table 1.1 lists the first five series of emission lines of hydrogen, which are named for their discoverers.

The work of Planck and Einstein showed that the energy of a photon was proportional to its frequency, so the discrete nature of the emission spectrum of atoms suggested that atoms may only transfer energy in the form of electromagnetic radiation at certain well-defined values, which depend only upon the identity of the element. Also, the regularity and simplicity of the Rydberg formula (Equation 1.5) suggested that a mathematical theory of the emission spectrum should be possible— at least for hydrogen.

The Bohr Model of the Hydrogen Atom

The basic building blocks of atoms were fairly well understood at the beginning of the twentieth century. Scientists knew that atoms consisted of negatively charged

Table 1.1	The First Five Spectral Series in the Emission Spectrum of Hydrogen		
Series	n_1	n_2	**Spectral Region**
Lyman	1	2, 3, 4, . . .	UV
Balmer	2	3, 4, 5, . . .	visible, UV
Paschen	3	4, 5, 6, . . .	IR
Brackett	4	5, 6, 7, . . .	IR
Pfund	5	6, 7, 8, . . .	IR

particles called electrons moving around a much heavier, compact nucleus. The nucleus consisted of positively charged particles called protons and some number of neutral particles called neutrons (see Section 0.2). In an atom, the number of electrons and protons was equal. Scientists thought of an atom as an entity in which electrons whirled around the nucleus in circular orbits at high velocities. This was an appealing model because it resembled the motions of the planets around the sun. In this model, the electrostatic attraction between the positively charged proton and the negatively charged electron pulls the electron inward. This force of attraction is balanced exactly by the acceleration due to the orbital motion of the electron.

This classical, planetary view of the atom was at odds with basic physics in two very important ways. First, Maxwell's theory of electromagnetism predicts that a charged particle will radiate energy when undergoing acceleration (this, in fact, is how radio waves are generated by a transmitter). Because of the electrostatic force of attraction between the electron and the protons of the nucleus, an electron revolving around a central nucleus is accelerated as it continually changes direction in its orbit. (Remember, acceleration is any change in the magnitude or direction of the velocity over time.) Thus, the electron would emit electromagnetic radiation with a frequency equal to the frequency of its orbital motion and would lose energy to the electromagnetic field. This continual loss of energy would cause the orbit to decay and the electron to quickly spiral into the nucleus. Thus, the classical atom would be inherently unstable and short lived—contrary to reality. Second, classical mechanics puts no restrictions on the orbital energy of the electron. Decreasing the orbital energy slightly only moves the electron to a slightly lower orbit. Thus, the emission spectrum of the classical atom should be continuous, and not discrete, as is observed.

Extending Planck's quantum hypothesis to the energies of atoms, the Danish physicist Niels Bohr[13] presented a new model of the atom that was able to account for the emission spectrum of hydrogen. Bohr used as his starting point the planetary model of the atom but modified it with restrictions that went beyond classical physics. For a single electron orbiting a nucleus containing Z protons, the ***Bohr model*** consists of the following assumptions:

1. The electron moves in a circular orbit about the nucleus.
2. The energy of the electron can take on only certain well-defined values; that is, it is quantized.
3. The only allowed orbits are those in which the magnitude of the ***angular momentum*** of the electron is equal to an integer multiple of $\hbar$, where $\hbar$ (called *h-bar*) is given by $\dfrac{h}{2\pi}$. The angular momentum of a particle (L) is a vector given by $\mathbf{L} = \mathbf{r} \times \mathbf{p},$ where r is the position vector of the particle, measured from the origin, $p = mu$ is the momentum of the particle (with mass m and velocity u), and "×" is the vector cross-product.
4. The electron can only absorb or emit electromagnetic radiation when it moves from one allowed orbit to another. The emitted radiation has an energy $h\nu$ equal to the difference in energy between the two orbits.

The first condition of the Bohr model is consistent with the classical model of the atom, but the rest were wholly original. By considering an electron orbiting a nucleus

Niels Bohr
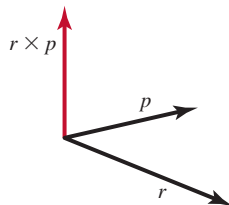
The cross product of two vectors is perpendicular to both.

13. Niels Henrik David Bohr (1885–1962). Danish physicist. One of the founders of modern physics, he received the Nobel Prize in Physics in 1922 for his theory explaining the spectrum of the hydrogen atom.

with Z protons, the Bohr model is not limited to the hydrogen atom ($Z = 1$), but can also describe any one-electron ion, called a ***hydrogenlike ion,*** such as He$^+$ ($Z = 2$), Li^{2+} ($Z = 3$), etc.

From these conditions, the allowed energies of the electron can be calculated. Coulomb's law (Equation 0.5) gives the potential energy, V, due to the interaction of two charged particles with charges q_1 and q_2, separated by a distance r:

$$V(r) = \frac{q_1 q_2}{4\pi\varepsilon_0 r} \tag{1.6}$$

where ε_0 is called the *permittivity of the vacuum* ($\varepsilon_0 = 8.854188 \times 10^{-12}$ C^2 J^{-1} m^{-1}). The attractive interaction between a nucleus of charge $+Ze$ and an electron of charge $-e$ at a distance r away is then

$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r} \tag{1.7}$$

Given a potential energy function, the force on the object is calculated as the negative of the derivative of the potential (see Appendix 1 for the definition of a derivative). For the electron in the atom, this force is

$$F(r) = -\frac{dV(r)}{dr} = -\frac{Ze^2}{4\pi\varepsilon_0 r^2}$$

According to Newton's second law (Equation 1.1), this force is equal to the mass of the electron (m_e) times its acceleration. For an electron in a circular orbit, the acceleration can be calculated to be $-u^2/r$, where u is the magnitude of the electron velocity, and the negative sign indicates that the acceleration is directed toward the nucleus. Newton's second law then gives

$$F = ma$$
$$-\frac{Ze^2}{4\pi\varepsilon_0 r^2} = -\frac{m_e u^2}{r}$$
$$\frac{Ze^2}{4\pi\varepsilon_0 r} = m_e u^2 \tag{1.8}$$

The total energy for the electron is the sum of the kinetic (Equation 0.3) and potential energies (Equation 1.7).

$$E = \frac{1}{2} m_e u^2 - \frac{Ze^2}{4\pi\varepsilon_0 r} \tag{1.9}$$

Substituting the orbit condition (Equation 1.8) into Equation 1.9 gives

$$E = \frac{1}{2} m_e u^2 - m_e u^2 = -\frac{1}{2} m_e u^2 \tag{1.10}$$

At this point, Bohr takes a bold step and postulates the quantum restriction that the angular momentum of the electron can only take on positive integer multiple values of $\hbar$ or $h/2\pi$. For an electron in a circular orbit, the angular momentum is $m_e r u$, so

$$m_e r\, u = n\hbar, \quad n = 1, 2, 3, \ldots \tag{1.11}$$

where n is referred to as a **quantum number.** Combining Equation 1.11 and Equation 1.8 gives

$$u = \frac{Ze^2}{2h\varepsilon_0 n} \tag{1.12}$$

If we substitute Equation 1.12 for u into the energy equation (Equation 1.10), we get the Bohr expression for the quantized energies, or **energy levels,** of the hydrogen atom.

$$E_n = -\frac{Z^2 e^4 m_e}{8h^2\varepsilon_0^2} \frac{1}{n^2} \quad n = 1, 2, 3, \dots \tag{1.13}$$

Because the zero of energy was (arbitrarily) defined in Equation 1.7 as the value at infinite separation of the electron from the nucleus (that is, where $n = \infty$), the negative sign in Equation 1.13 implies that all of these states are lower in energy than an infinitely separated proton and electron pair. We call such states the *bound states* of the atom. The most stable state is given by the lowest energy level and is called the **ground state** (or *ground level*), which for the Bohr model corresponds to $n = 1$. The higher energy levels are referred to as **excited states** (or *excited levels*). For the hydrogen atom ($Z = 1$), the ground-state energy is

$$E_1 = -\frac{m_e e^4}{8h^2\varepsilon_0^2} = -2.185 \times 10^{-18} \text{ J}$$

The negative of this energy, $+2.185 \times 10^{-18}$ J (or 1316 kJ mol^{-1}), is the amount of energy that is needed to completely remove the electron from a ground-state hydrogen atom. This process is called **ionization,** and the energy required for ionization is called the **ionization energy.**

Equations 1.11 and 1.12 can also be used to derive the following expression for the radius of the Bohr orbits:

$$r_n = \frac{\varepsilon_0 h^2 n^2}{Z\pi m_e e^2} \quad n = 1, 2, 3, \dots \tag{1.14}$$

Thus, like the energy, the orbit radius is quantized and can only take on certain values, which increase proportional to n^2. The value of the radius for the ground state ($n = 1$), calculated in Example 1.4, is called the **Bohr radius** (a_0).

Example 1.4

Calculate the Bohr radius of the ground state ($n = 1$) of the hydrogen atom.

Strategy Use Equation 1.14 with $Z = 1$ (for hydrogen) and $n = 1$ (for the ground state). The other constants in the equation can be found inside the back cover of the book.

Solution Start with Equation 1.14 with $n = Z = 1$:

$$a_0 = \frac{\varepsilon_0 h^2}{\pi m_e e^2}$$

—Continued

Continued—

Now substitute in the values of ε_0, h, m_e, and e:

$$a_0 = \frac{(8.8542 \times 10^{-12} \text{C}^2 \text{J}^{-1} \text{m}^{-1})(6.626 \times 10^{-34} \text{J s})^2}{\pi(9.109 \times 10^{-31} \text{kg})(1.602 \times 10^{-19} \text{C})^2}$$

$$= 5.29 \times 10^{-11} \text{ m}$$

$$= 52.9 \text{ pm}$$

where we have used the conversion factors $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$ and $1 \text{ pm} = 10^{-12}$ m. More commonly the Bohr radius is expressed as 0.529 Å. The Bohr radius is generally given the symbol a_0.

Practice Exercise Calculate the radius for the first excited state ($n = 2$) of the He^+ ion.

How does Equation 1.13 account for the line spectrum of hydrogen? Radiant energy absorbed by the atom causes the electron to move from a lower-energy quantum state (characterized by a smaller n value) to a higher-energy quantum state (characterized by a larger n value). Conversely, radiant energy (in the form of a photon) is emitted when the electron moves from a higher-energy quantum state to a lower-energy quantum state (Figure 1.14). The conservation of energy requires that the energy of the photon emitted or absorbed be equal to the change in the energy of the electron—that is, equal to the difference in energy (ΔE) between the initial and final energy levels. Consider the case of emission and let n_2 represent the value of the quantum number n in the initial state and n_1 be that of the final state, with $n_2 > n_1$. The energy of the emitted photon is given by

$$E_{\text{photon}} = h\nu = \Delta E = E_{n_2} - E_{n_1}$$

Using Equation 1.13, this gives

$$E_{\text{photon}} = h\nu = \frac{Z^2 e^4 m_e}{8h^2 \varepsilon_0^2}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \tag{1.15}$$

or

$$\nu = \frac{Z^2 e^4 m_e}{8h^3 \varepsilon_0^2}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] = Z^2 R_{\text{H}}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \tag{1.16}$$

Setting $Z = 1$, we see that Equation 1.16 is identical to Rydberg's empirical equation for the hydrogen emission spectrum (Equation 1.5) and gives an expression for the Rydberg constant in terms of fundamental physical constants:

$$R_{\text{H}} = \frac{e^4 m_e}{8h^3 \varepsilon_0^2} = 3.289832496 \times 10^{15} \text{ s}^{-1} \tag{1.17}$$

The value of R_{H} calculated from Equation 1.17 is nearly[14] identical to the experimentally determined value! Equation 1.16 was derived for the case of emission of a photon. For absorption, we have $n_1 > n_2$, so the sign of the frequency would be

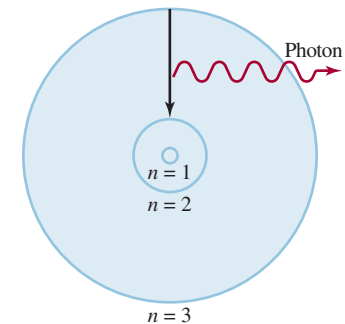**Figure 1.14** The emission process in an excited hydrogen atom, according to Bohr's theory. An electron originally in a higher-energy orbit ($n_2 = 3$) falls back to a lower-energy orbit ($n_1 = 2$). As a result, a photon with energy $h\nu$ is given off. The value of $h\nu$ is equal to the difference in energy between the initial and final electron orbits. For simplicity, only three orbits are shown.

14. See Problem 1.60.

Figure 1.15 The energy levels in the hydrogen atom and the various emission series. Each energy level corresponds to the energy associated with an allowed quantum state for an orbit, as postulated by Bohr and as shown in Figure 1.14. The emission lines are labeled according to the scheme in Table 1.1.
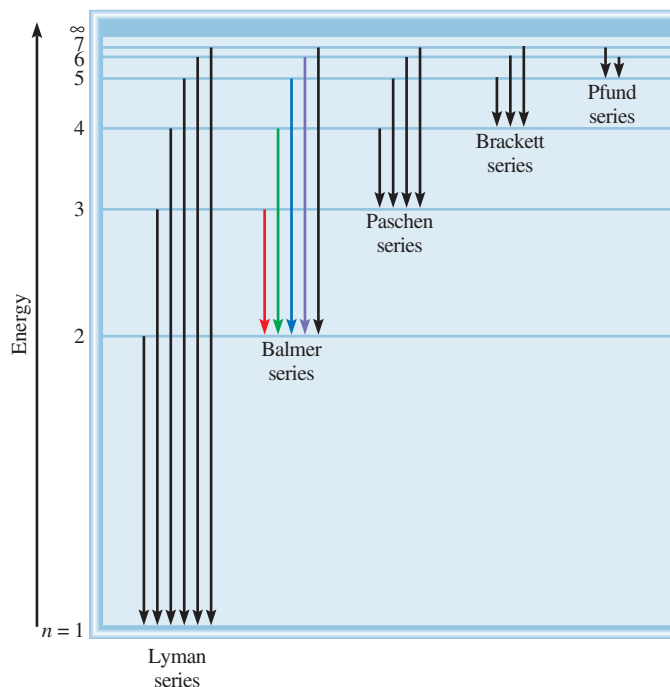
negative (see Equation 1.15), which is not physically meaningful. To ensure that the frequency of transition (whether emission or absorption) is positive, we can take the *absolute value* of $[(1/n_1^2) - (1/n_2^2)]$ in Equation 1.15.

Figure 1.15 shows the various energy levels of the hydrogen atom and the transitions that correspond to the spectral series shown in Table 1.1.

Example 1.5

What is the wavelength of a photon (in nanometers) emitted during a transition from the $n_2 = 5$ state to the $n_1 = 2$ state in the hydrogen atom? To what region of the electromagnetic spectrum does this wavelength correspond?

Strategy We are given the initial and final states in the emission process. We can calculate the frequency of the emitted photon using Equation 1.16. From Equation 1.2 (using the speed of light c as the speed of the wave), we can then calculate the wavelength from the frequency. The region of the electromagnetic spectrum to which the calculated wavelength belongs can be found by consulting Figure 1.6.

Solution From Equation 1.16 we write

$$\nu = R_H Z^2 \left| \frac{1}{n_1^2} - \frac{1}{n_2^2} \right|$$

where the vertical lines indicate that we have used the absolute value to ensure that our frequencies are positive. The Rydberg constant is 3.28983×10^{15} s^{-1} and for hydrogen $Z = 1$, so

$$\nu = 3.28983 \times 10^{15} \text{ s}^{-1} (1)^2 \left| \frac{1}{2^2} - \frac{1}{5^2} \right|$$

$$\nu = 6.90864 \times 10^{14} \text{ s}^{-1}$$

—Continued

Continued—
From Equation 1.2, we have

$$\lambda = \frac{c}{\nu} = \frac{2.99879 \times 10^8 \text{ m s}^{-1}}{6.90864 \times 10^{14} \text{ s}^{-1}}$$

$$= 4.34064 \times 10^{-7} \text{ m} \times \left(\frac{1 \times 10^9 \text{ nm}}{1 \text{ m}} \right)$$

$$= 434.064 \text{ nm}$$

According to Figure 1.6, this wavelength lies in the *visible* region of the electromagnetic spectrum, specifically in the violet/indigo range of the visible spectrum.

Practice Exercise For He$^+$ ($Z = 2$), calculate the wavelength of light (in nm) absorbed when an electron in the $n = 3$ state is excited to the $n = 6$ level. To what region of the electromagnetic spectrum does this wavelength correspond?

Bohr's idea that the energy states of matter, like light, are quantized was subsequently supported by a series of experiments performed by James Franck[15] and Gustav Hertz[16] in the decade following Bohr's hypothesis. Franck and Hertz collided fast moving electrons with atoms. (Figure 1.16(a) is an illustration of their apparatus.) At low

15. James Franck (1882–1964). German physicist and physical chemist. In addition to his work with Gustav Hertz confirming the existence of energy levels in atoms, he made numerous contributions to the field of photochemistry. He shared the 1925 Nobel Prize in Physics with Gustav Hertz.

16. Gustav Hertz (1887–1975). German physicist. He made major advances in the field of gas-phase spectroscopy and in the separation of isotopes. He shared the 1925 Nobel Prize in Physics with Franck for his work supporting the Bohr hypothesis of energy quantization in matter.

Anode (controls electron energy)   Electron beam   Electron collector plate

Electron source (cathode)   Gas atoms

(a)

Threshold voltage
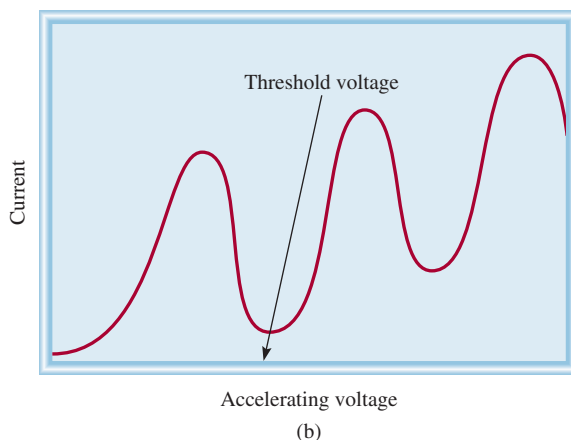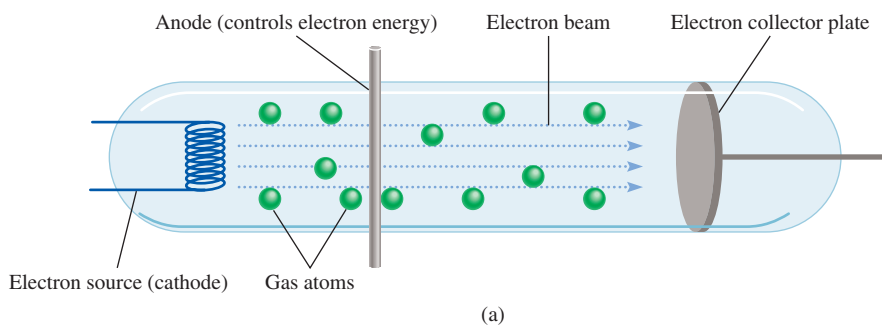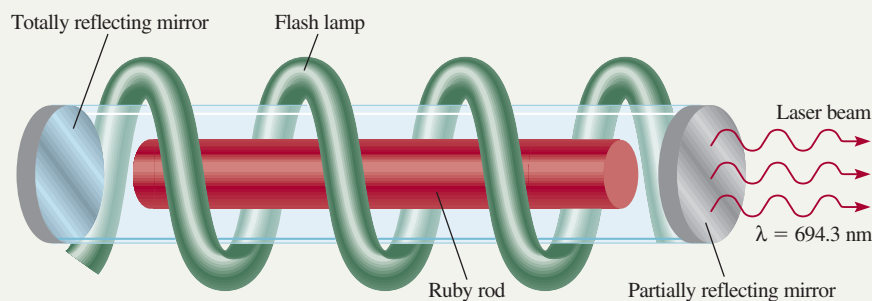
Current

Accelerating voltage

(b)

Figure 1.16 The Frank-Hertz experiment: (a) The apparatus. (b) Plot of the current through the tube as a function of accelerating voltage.
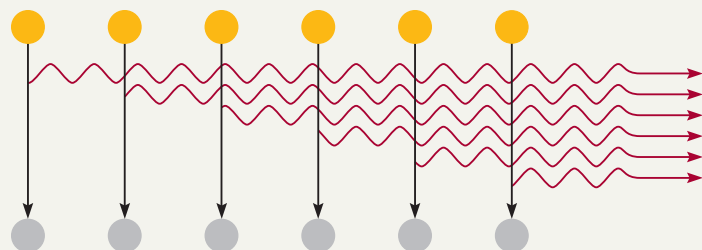
Laser—The Splendid Light

Laser is an acronym for *l*ight *a*mplification by *s*timulated *e*mission of *r*adiation. It is a special type of emission that involves either atoms or molecules. Since the discovery of laser in 1960, it has been used in numerous systems designed to operate in the gas, liquid, and solid states. These systems emit radiation with wavelengths ranging from infrared through visible and ultraviolet. The advent of laser has truly revolutionized science, medicine, and technology.

Ruby laser was the first known laser. Ruby is a deep-red mineral containing corundum, Al_2O_3, in which some of the Al^{3+} ions have been replaced by Cr^{3+} ions. A flashlamp is used to excite the chromium atoms to a higher energy level. The excited atoms are unstable, so at a given instant some of them return to the ground state by emitting a photon in the red region of the spectrum. The photon bounces back and forth many times between mirrors at opposite ends of the laser tube.

Totally reflecting mirror   Flash lamp

Laser beam

$\lambda = 694.3$ nm

Ruby rod   Partially reflecting mirror

The emission of a laser light from a ruby laser.

The stimulated emission of one photon in a cascade event that leads to the emission of laser light. The synchronization of the light waves produces an intensely penetrating laser beam.

collision energies, the electrons were scattered by the collisions with the atoms, but experienced no loss of kinetic energy. However, when the initial kinetic energy of the electrons was increased beyond a critical value, the electrons exhibited a large loss of kinetic energy in the collision with an atom [Figure 1.16(b)]. These experiments showed that a certain minimum energy was needed to transfer energy from the electron to the atom. Within the Bohr hypothesis these results can be explained as follows: If the kinetic energy of the electron is smaller than the difference in energy, ΔE, between the ground state and the first excited state of the atom, the atom cannot absorb the energy. However, once the kinetic energy of the electron exceeds this value, energy transfer is possible and the kinetic energy of the electron is reduced by ΔE. As the initial kinetic energy of the electrons is increased further, additional dips in their postcollision kinetic energy are expected to appear as the higher excited state energies of the atom are reached—and this is exactly what was seen in the Franck-Hertz experiments.

In spite of its initial success in explaining the spectrum of the hydrogen atom and hydrogenlike ions, the Bohr model had a number of deficiencies. First, as more accurate spectra of the hydrogen atom became available, many of the lines previously seen to be single lines turned out on close inspection to be closely spaced pairs of lines (called *doublets*). The Bohr model, with its single quantum number n, was neither able to account for this *fine structure* of the atomic spectrum nor able to explain the changes induced in

This photon can stimulate the emission of photons of exactly the same wavelength from other excited chromium atoms; these photons in turn can stimulate the emission of more photons, and so on. Because the light waves are *in phase*—that is, their maxima and minima coincide—the photons enhance one another, increasing their power with each passage between the mirrors. One of the mirrors is only partially reflecting, so that when the light reaches a certain intensity it emerges from the mirror as a laser beam. Depending on the mode of operation, the laser light may be emitted in pulses (as in the ruby laser case) or in continuous waves.

Laser light is characterized by three properties: It is intense, it has precisely known wavelength and hence energy, and it is coherent. By *coherent* we mean that the light waves are all in phase. The applications of lasers are numerous. Their high intensity and ease of focus make them suitable for doing eye surgery, for welding and drilling holes in metals, and for carrying out nuclear fusion. Because they are highly directional and have precisely known wavelengths, they are very useful for telecommunications. Lasers are also used in isotope separation, in holography (three-dimensional photography), in compact disc players, and in supermarket scanners. Lasers have played an important role in the spectroscopic investigation of molecular properties and of many chemical and biological processes. Laser lights are increasingly being used to probe the details of chemical reactions (see Chapter 13).
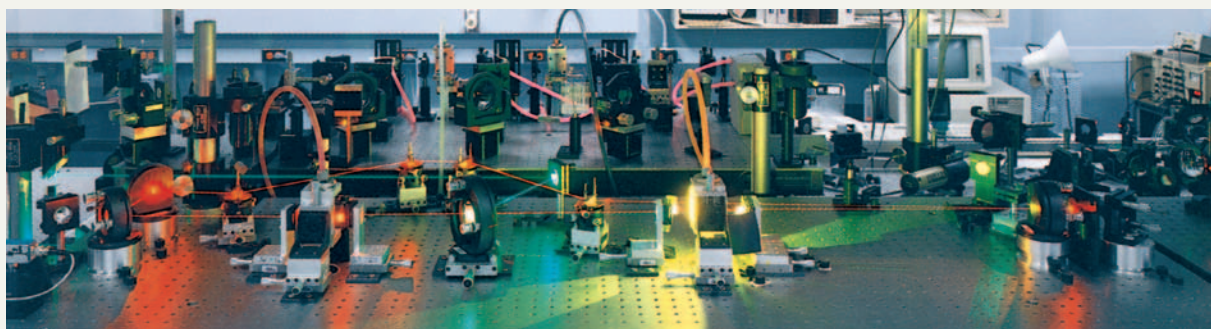
State-of-the-art lasers used in the research laboratory of Dr. A. H. Zewail at the California Institute of Technology.

the spectrum when a magnetic field was applied. In 1916 the German physicist Arnold Sommerfeld[17] rectified these problems by extending the Bohr model by taking into account Einstein's special theory of relativity and included elliptical orbits through the introduction of additional quantization conditions and quantum numbers. This more complete theory is generally referred to as the Bohr-Sommerfeld model of the atom or simply as "Old Quantum Theory." Second, and more serious, was the complete failure of the Bohr-Sommerfeld theory to accurately predict spectral lines in atoms with more than one electron, even those as simple as helium. It became clear that a more general theory was needed to account for atoms other than hydrogen. As we shall see, the problem with the Bohr-Sommerfeld theory was not that it was "wrong." Instead, the real failings of the theory occured because it did not go far enough in moving away from the precepts of classical theory. In the Bohr-Sommerfeld model, the electrons were still viewed as classical point particles orbiting the nucleus, with a well-defined position and a well-defined momentum at all times. As we will see in Section 1.3, the electrons in an

17. Arnold Johannes Wilhelm Sommerfeld (1868–1951). German physicist. In addition to his pioneering work on the relationship between atomic structure and spectral lines, he made important contributions to understanding the electronic properties of metals.

atom are more accurately described as wavelike objects for which position and momentum cannot be simultaneously defined with precision.

Despite its shortcomings, however, the Bohr-Sommerfeld model is of enormous significance in the development of the quantum theory and, in a broader sense, as an illustration of the evolution of scientific ideas.

1.3 | Matter Has Wavelike Properties

Physicists were both mystified and intrigued by Bohr's theory and sought to understand *why* the energy levels would be quantized. That is, why is the electron in a Bohr atom restricted to orbiting the nucleus at certain fixed distances? For a decade no one, not even Bohr himself, had a logical explanation. In 1924, though, Louis de Broglie[18] provided a solution to this puzzle.

The Wave-Particle Duality of Matter—The de Broglie Hypothesis

De Broglie reasoned that if light waves could behave like a stream of particles (photons), then perhaps particles such as electrons could possess wavelike properties. To quantify this connection, de Broglie began with the expression (from Einstein's theory of special relativity) for the momentum (p) of the photon:

$$p = E/c \tag{1.18}$$

where E is the energy of the photon and c is the speed of light. Combining this equation with the Einstein–Planck expression for the photon energy in terms of its frequency (Equation 1.3) and the relationship (from Equation 1.2) between frequency and wavelength, ($\nu = c/\lambda$), we obtain, after rearrangement,

$$p = \frac{h\nu}{c} = \frac{h}{\lambda}$$

Louis de Broglie

or

$$\lambda = \frac{h}{p} \tag{1.19}$$

Equation 1.19 was derived using equations applicable to the photon, which is massless and has a fixed velocity c. De Broglie postulated that the equation should also apply to particles of matter with mass m and velocity u. Substituting the expression for the momentum of a particle ($p = mu$) into Equation 1.19 gives the de Broglie relation for the wavelength of a particle:

$$\lambda = \frac{h}{mu} \tag{1.20}$$

The wavelength defined in Equation 1.20 is called the ***de Broglie wavelength*** of a particle. Equation 1.20 implies that a particle in motion can be treated as a wave and that a wave can exhibit the properties of a particle (that is, its momentum). Thus, the left side of Equation 1.20 addresses the wavelike properties of matter (wavelength), whereas the right side addresses its particle-like properties (mass).

18. Louis Victor Pierre Raymond duc de Broglie (1892–1987). French physicist. Member of an old and noble family in France, he held the title of a prince. In his doctoral dissertation, he proposed that matter and radiation have the properties of both waves and particles. For this work, de Broglie was awarded the Nobel Prize in Physics in 1929.

Example 1.6

Calculate the wavelength of the "particle" in the following two cases: (a) A 6.0×10^{-2} kg tennis ball served at 140 miles per hour (63 m s^{-1}). (b) An electron ($m_e = 9.1094 \times 10^{-31}$ kg) moving at 63 m s^{-1}.

Strategy We are given the mass (m) and the speed (u) of the particle in (a) and (b) and asked to calculate the wavelength (λ). We can use Equation 1.20 to do this. Note, however, that Planck's constant has units of J s, so m and u must be in units of kg and m s^{-1}, respectively (1 J = 1 kg m^2 s^{-2}).

(a) Solution Using Equation 1.20 for the tennis ball we write

$$\lambda = \frac{h}{mu}$$
$$= \frac{6.626 \times 10^{-34} \text{ J s}}{(6.0 \times 10^{-2} \text{ kg})(63 \text{ m s}^{-1})}$$
$$= 1.8 \times 10^{-34} \text{ m}$$

Comment This is an exceedingly small wavelength considering that the size of an atom itself is on the order of 1×10^{-10} m. For this reason, the wave properties of a tennis ball cannot be detected by any existing measuring device.

(b) Solution For the electron,

$$\lambda = \frac{h}{mu}$$
$$= \frac{6.626 \times 10^{-34} \text{ J s}}{(9.1094 \times 10^{-31} \text{ kg})(63 \text{ m s}^{-1})}$$
$$= 1.2 \times 10^{-5} \text{ m}$$

Comment This wavelength (1.2×10^{-5} m or 1.2×10^4 nm) is in the infrared region and is much larger than the size of an atom. This calculation shows that only submicroscopic particles (such as electrons) have measurable wavelengths.

Practice Exercise Calculate the wavelength (in nanometers) of a hydrogen atom (mass = 1.674×10^{-27} kg) moving at 7.00×10^2 cm s^{-1}.

Example 1.6 shows that although de Broglie's equation can be applied to diverse systems, the wave properties become observable only for submicroscopic objects. This distinction occurs because Planck's constant, h, which appears in the numerator in Equation 1.20, is so small.

According to de Broglie, an electron bound to the nucleus behaves like a ***standing wave***. Standing waves can be generated by plucking a guitar string (Figure 1.17). The waves are described as standing, or stationary, because they do not travel along the string. Some points on the string, called ***nodes,*** do not move at all; that is, *the amplitude of the wave at these points is zero.* There is a node at each end, and there may be nodes between the ends. The greater the frequency of vibration, the shorter the
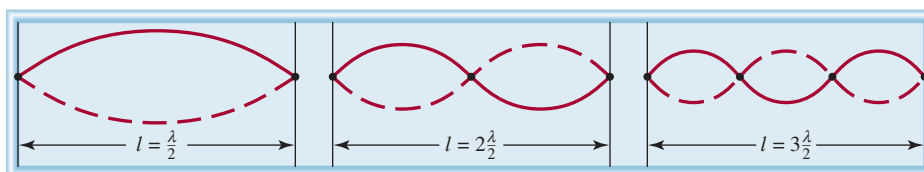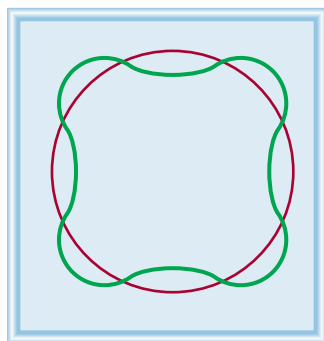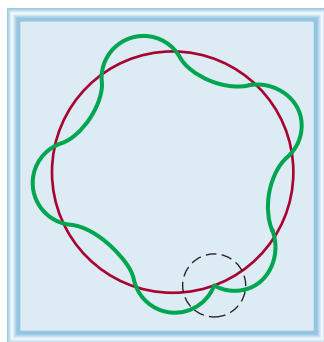

Figure 1.17 The standing waves generated by plucking a guitar string. Each dot represents a node. The length of the string, *l*, must be equal to a whole number times one-half the wavelength ($\lambda/2$).

(a)

(b)

Figure 1.18 (a) The circumference of the orbit is equal to an integral number of wavelengths. This is an allowed orbit. (b) The circumference of the orbit is not equal to an integral number of wavelengths. As a result, the electron wave does not close in on itself. This is a nonallowed orbit.

wavelength of the standing wave and the greater the number of nodes. As Figure 1.17 shows, there can be only certain wavelengths in any of the allowed motions of the string. *The existence of discrete energy states is the natural consequence of confining a wavelike object to a finite region of space.*

De Broglie argued that if an electron does behave like a standing wave in the hydrogen atom, the length of the wave must fit the circumference of the orbit exactly (Figure 1.18)—otherwise the wave would partially cancel itself on each successive orbit. Eventually the amplitude of the wave would be reduced to zero, and the wave would cease to exist. The relation between the circumference of an allowed orbit ($2\pi r$) and the de Broglie wavelength (λ) of the electron is given by

$$2\pi r = n\lambda \quad n = 1, 2, 3, \ldots \quad \textbf{(1.21)}$$

where r is the radius of the orbit and λ is the wavelength of the electron wave. Using Equation 1.21 together with the expression for λ in Equation 1.20, we obtain

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

Upon rearrangement,

$$m_e u r = \frac{nh}{2\pi} = n\hbar \quad n = 1, 2, 3, \ldots$$

which is identical to the Bohr angular momentum condition expressed in Equation 1.11. Thus, de Broglie's postulate leads to quantized angular momentum and to the quantized energy levels of the hydrogen atom.

Shortly after de Broglie introduced his equation, Clinton Davisson[19] and Lester Germer[20] in the United States and G. P. Thomson[21] in England demonstrated that electrons do indeed possess wavelike properties. By directing a beam of electrons at a thin piece of gold foil, Thomson obtained a set of concentric rings on a detector screen, similar to the pattern observed when X-rays (which are waves) were used. Figure 1.19 shows the same kind of pattern for aluminum. The wavelike nature of electron beams has application in a number of experimental techniques, such as *electron microscopy* (discussed in the inset on page 109) and *low energy electron diffraction (LEED),* which is used to study the surfaces of crystalline solids. Another technique, *neutron diffraction,* uses the wavelike properties of neutrons to study the structure and dynamics of dense materials, such as liquids.

The Heisenberg Uncertainty Principle

One of the assumptions of classical physics is that the dynamical variables (positions and momenta) of a particle in motion have well-defined, precise values. However, the concept of a precise position becomes ill-defined when we try to describe a particle as a wavelike object. A wave is an object that is extended over some region of space. To describe the problem of trying to locate a subatomic particle that behaves like a wave, Werner

19. Clinton Joseph Davisson (1881–1958). American physicist. He and G. P. Thomson shared the Nobel Prize in Physics in 1937 for demonstrating the wave properties of electrons.

20. Lester Halbert Germer (1896–1972). American physicist. Discoverer (with Davisson) of the wave properties of electrons.

21. George Paget Thomson (1892–1975). English physicist. Son of J. J. Thomson, he received the Nobel Prize in Physics in 1937, along with Clinton Davisson, for demonstrating the wave properties of electrons.
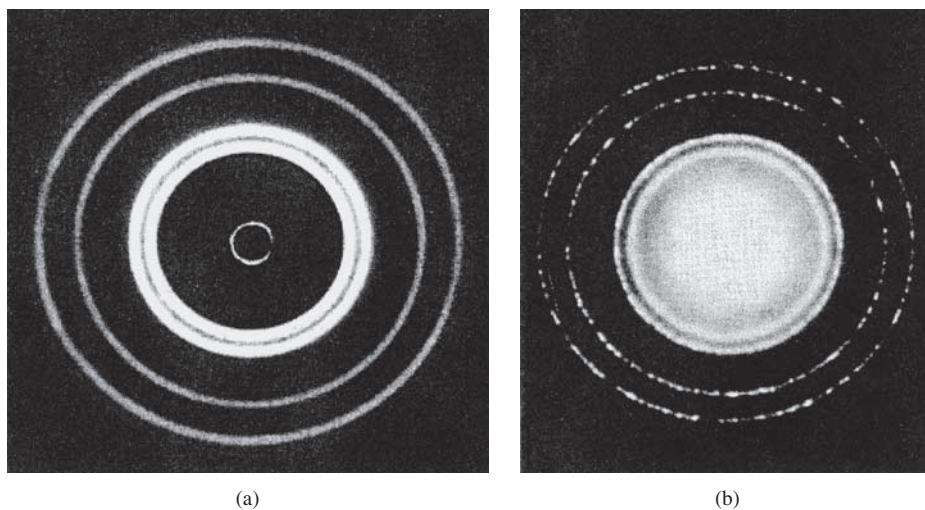
(a)   (b)

Heisenberg[22] formulated what is now known as the ***Heisenberg uncertainty principle:*** *It is impossible to know simultaneously both the momentum p* (defined as mass times velocity) *and the position of a particle with certainty.* Stated mathematically we have,

$$\Delta x \, \Delta p \geq \frac{\hbar}{2}$$

(1.22)

where Δx and Δp are the uncertainties in measuring the position and momentum, respectively. Thus, if we measure the momentum of a particle more precisely (that is, if we make Δp a small quantity), our knowledge of the position will become correspondingly less precise (that is, Δx will become larger). Similarly, if the position of the particle is known more precisely, then its momentum must be known less precisely. This inverse relationship arises because the position of a wavelike particle is determined by the region of space occupied by the wave, but the momentum, through the de Broglie relationship, is related to the wavelength of the wave.

Figure 1.20 depicts two extreme cases. In Figure 1.20(a) a wave is extended over a large region of space; however, the wavelength of the wave is well defined. Such a particle-wave would have a small uncertainty in the momentum (wavelength), but a large uncertainty in the position. In Figure 1.20(b), on the other hand, the wave is

Werner Heisenberg

22. Werner Karl Heisenberg (1901–1976). German physicist. One of the founders of modern quantum theory. Heisenberg received the Nobel Prize in Physics in 1932.

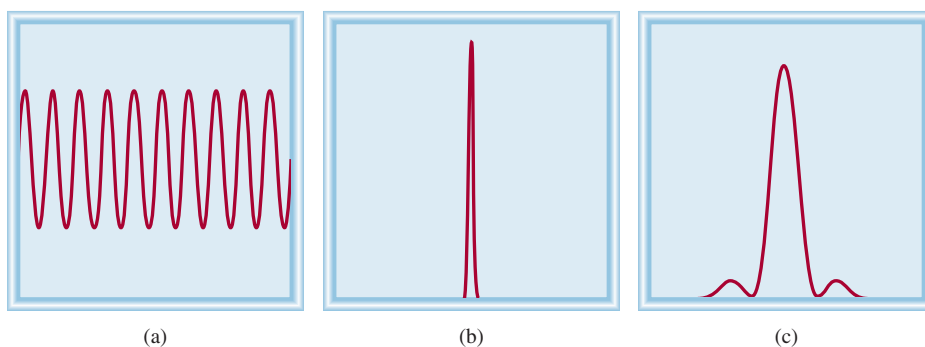(a)   (b)   (c)

Figure 1.20 Three illustrations of the Heisenberg uncertainty principle. (a) A particle-wave with a large uncertainty in position, but with a well-defined wavelength (momentum). (b) A particle-wave with a well-defined position, but a large uncertainty in wavelength (momentum). (c) A particle-wave with intermediate uncertainty in position and momentum.

highly localized in space (giving a small value of Δx). but the wavelength is difficult to define; that is, it has a large uncertainty in the wavelength. Figure 1.20(c) shows a wave that is intermediate between the two extremes in Figure 1.20(a) and 1.20(b).

When the Heisenberg uncertainty principle is applied to the hydrogen atom, it is found that the electron cannot orbit the nucleus in a well-defined path, as Bohr thought. If it did, we could determine precisely both the position of the electron (from the radius of the orbit) and its momentum (from its kinetic energy) at the same time, a violation of the uncertainty principle.

The uncertainty principle is negligible in the world of macroscopic objects (because of the small size of Planck's constant), but is very important for objects with small masses, such as electrons and protons.

Example 1.7

Recall from Example 1.4 that the Bohr radius of the hydrogen atom is 52.9 pm (or 0.529Å). Assuming that we know the position of an electron in this orbit to an accuracy of 1 percent of the radius, calculate the uncertainty in the velocity of the electron.

Strategy   The uncertainty, Δx, in the position of the electron is given. From the Heisenberg uncertainty principle (Equation 1.22), we can calculate the minimum uncertainty in the momentum, Δp, from which the uncertainty in the velocity can be determined.

Solution   The uncertainty, Δx, in the position of the electron is

$$\Delta x = \frac{1\%}{100\%} \times 52.9 \text{ pm} \times \frac{1 \times 10^{-12} \text{ m}}{1 \text{ pm}} = 5.29 \times 10^{-13} \text{ m}$$

From the Heisenberg uncertainty principle (Equation 1.22), we have

$$\Delta p \geq \frac{\hbar}{2\Delta x} = \frac{1.054 \times 10^{-34} \text{ J s}}{2(5.29 \times 10^{-13} \text{ m})}$$
$$\geq 9.96 \times 10^{-23} \text{ kg m s}^{-1}$$

Because $\Delta p = m\,\Delta u$, the uncertainty in the velocity is given by

$$\Delta u = \frac{\Delta p}{m} \geq \frac{9.96 \times 10^{-23} \text{ kg m s}^{-1}}{9.1095 \times 10^{-31} \text{ kg}}$$
$$\geq 1.1 \times 10^{8} \text{ m s}^{-1}$$

The uncertainty in the velocity of the electron is of the same magnitude as the speed of light (3×10^{8} m s^{-1}). At this level of uncertainty, we have virtually no idea what the velocity of the electron is.

Practice Exercise   Repeat the calculation in Example 1.7 using a proton instead of an electron.

The Schrödinger Wave Equation

The de Broglie relation and the Heisenberg uncertainty principle successfully demonstrated the major flaw in the Bohr-Sommerfeld model. Although Bohr went beyond classical physics in postulating the quantization of energy levels, his theory still relied

on the Newtonian notion of particle trajectories. In the Bohr-Sommerfeld orbits both the momentum and position of the electron had specific well-defined values at all times, in violation of the Heisenberg uncertainty principle. De Broglie postulated that a particle has wavelike properties, but his theory was incomplete, as it did not provide a quantitative determination of the properties of such a system. A general equation was needed for quantum systems, one comparable in predictive power to Newton's second law of motion for classical objects. In 1926, the Austrian physicist Erwin Schrödinger[23] furnished the necessary equation.[24]

In classical mechanics, the state of a particle is defined uniquely by its position and momentum. If you know both of these quantities, then you can predict the future motion of the particle based on the forces acting upon it. According to Heisenberg's uncertainty principle, though, this sort of knowledge is unavailable for a quantum particle, as the position and momentum cannot be simultaneously specified. *Schrödinger postulated that the complete information about the state of a quantum particle was contained in a function $\psi(x)$*, called the **wavefunction**, which is a function of the position of the particle (given by x for a one-dimensional system). One of the most important properties of wavelike objects is the ability to exhibit constructive and destructive interference. For this to be possible, the wave function must be able to take on positive *or* negative values.

We know from everyday experience what is meant by the classical state of a particle—that is, by position and momentum. But what is meant by ψ? The currently accepted physical interpretation of ψ, given in 1926 by German physicist Max Born,[25] is that the wavefunction is related to the *probability* of finding the particle in a specific region of space. Because ψ can take on negative values, and probability is, by definition, a positive quantity, Born postulated that the probability of finding the particle in a particular small region of space was proportional to the *square* of the wavefunction. Specifically, for a one-dimensional system, the probability of finding the particle between positions x and $x + dx$ is given by $\psi^2(x)\,dx$.[26] As shown in Figure 1.21, the probability, P, of finding the particle in a specific region $a < x < b$ is given by the area under the curve, $\psi^2(x)$, between $x = a$ and $x = b$ (which can be calculated from the integral of $\psi^2(x)$ on this interval):

$$P = \text{area under } \psi^2(x) \text{ from } a \text{ to } b$$
$$= \int_a^b \psi^2(x)\,dx \tag{1.23}$$

(Because the probability of finding the particle in a specific region of space is not given directly by $\psi^2(x)$, but instead by an integral of $\psi^2(x)$ over the region, we refer to $\psi^2(x)$ not as a probability, but as a *probability density*).

Erwin Schrödinger

23. Erwin Schrödinger (1887–1961). Austrian physicist. Schrödinger formulated wave mechanics, which laid the foundation for modern quantum mechanics. He received the Nobel Prize in Physics in 1933.

24. An alternative formulation of quantum mechanics, based on matrices, was developed independently by Heisenberg at about the same time. It was later shown that this "matrix mechanics" is equivalent to Schrödinger's theory.

25. Max Born (1882–1970). German physicist. In addition to being one of the pioneers in modern quantum mechanics, he made major contributions to electrodynamics and the theory of crystals. He received the Nobel Prize in Physics in 1953.

26. Mathematically, the wavefunction can be a complex number, such as $A + iB$ where $i = \sqrt{-1}$. To be physically meaningful, this probability should be given as $\psi^*(x)\psi(x)$, where $\psi^*(x)$ is the *complex conjugate* of $\psi(x)$. If $\psi(x)$ is written as $A + iB$, where A and B are real, then $\psi^*(x)$ is defined as $A - iB$ and $\psi^*(x)\psi(x) = (A + iB)(A - iB) = A^2 + B^2$. This is necessary to ensure that the probability density $\psi^*(x)\psi(x)$ is always positive. If $\psi(x)$ is a real number, then $\psi^*(x) = \psi(x)$ and $\psi^*(x)\psi(x) = \psi^2(x)$, the usual square.

Figure 1.21 (a) An example of a wavefunction [$\psi(x)$] for a particle in a one-dimensional system as a function of position (x). (b) The probability density [$\psi^2(x)$] defined by the wavefunction in (a). The probability of the particle being in the interval ($a < x < b$) is given by the area under the curve over this interval (shaded).

(a)

(b)
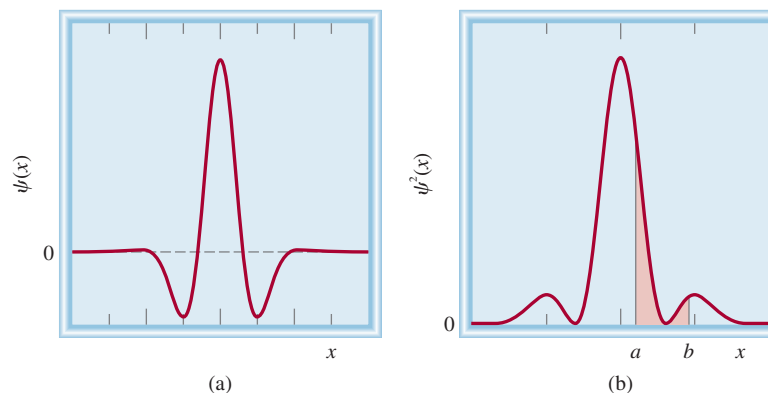
In quantum mechanics, we *cannot* specify the exact position of the particle, only the probability that it will be found in some region of interest. This has nothing to do with the inadequacy of our measuring devices—it is a fundamental property of matter!

By analogy with the laws of optics, Schrödinger proposed that the wavefunction for a particle of mass m in one dimension is the solution to the equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \qquad (1.24)$$

where $V(x)$ is the potential energy function and E is the total energy. Like Newton's second law of classical mechanics, the Schrödinger equation (Equation 1.24) is a *postulate* and cannot be derived. The Schrödinger equation marked the beginning of a new era in physics—that of wave mechanics or **quantum mechanics.**

Equation 1.24 does not contain time as a variable and is referred to as the ***time-independent Schrödinger equation*.** The wavefunctions that are the solutions to Equation 1.24 do not change with time and are called *stationary-state* wavefunctions.[27] For a specific system, the Schrödinger equation can be solved only for certain values of E; that is, the energy of the system is quantized.

To describe a physical system, the wavefunction (ψ) must also be "well-behaved"; that is, it must satisfy the following conditions:

1. ψ must be single-valued at all points.

2.   The total area under $\psi^2(x)$ must be equal to unity; that is, $\int_{-\infty}^{\infty}\psi^2(x)\,dx = 1$.

3. ψ must be "smooth"; that is, ψ and its first derivative (slope), $d\psi/dx$, must be continuous at all points.

The first condition ensures that the probability of finding the particle in a given region of space has a unique value. The second condition is a statement that the probability of finding the particle somewhere is equal to one; that is, the particle exists. The third condition is necessary so that the second derivative of ψ, which appears in Equation 1.24, is physically meaningful.

27. A more general equation containing time as a variable was also formulated by Schrödinger and is useful in the description of spectroscopic techniques. However, many problems of chemical interest can be adequately described using only the stationary-state wavefunctions.

For an arbitrary system, the solution to the Schrödinger equation can be quite complex. However, it is possible by examining the form of the Schrödinger equation to deduce some qualitative aspects of the wavefunction. The left-hand side of Equation 1.24 contains two terms. The first term,

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}$$

represents the *kinetic energy* part of the equation. This term is proportional to the second derivative of the wave function ($d^2\psi/dx^2$), which describes the *curvature* of the wavefunction (see Appendix 1). Thus, wavefunctions with high curvature have high kinetic energy and those that are relatively flat (low curvature) have low kinetic energy. The second term on the left-hand side of Equation 1.24,

$$V(x)\psi(x)$$

describes the potential energy of the system. Consider the wavefunction for the ground state (lowest energy state) of a given system. (Figure 1.22) The wavefunction of minimum potential energy would be one in which the probability density (and, thus, the wavefunction) for the particle is narrowly peaked in the vicinity of the potential energy minimum [Figure 1.22(b)]. Such a wavefunction, however, would have a high curvature and thus a high kinetic energy. Lowering the kinetic energy involves decreasing the curvature of the wavefunction (that is, spreading it out more over space), which allows the particle to exist in regions that have high potential energy. [Figure 1.22(c)] The true ground-state wavefunction of a particle represents a *compromise* between these two extremes [Figure 1.22(d)].

The Particle in a One-Dimensional Box: A Simple Model

For most problems in nature, the Schrödinger wave equation cannot be solved exactly, and we must use sophisticated computer algorithms to obtain even approximate

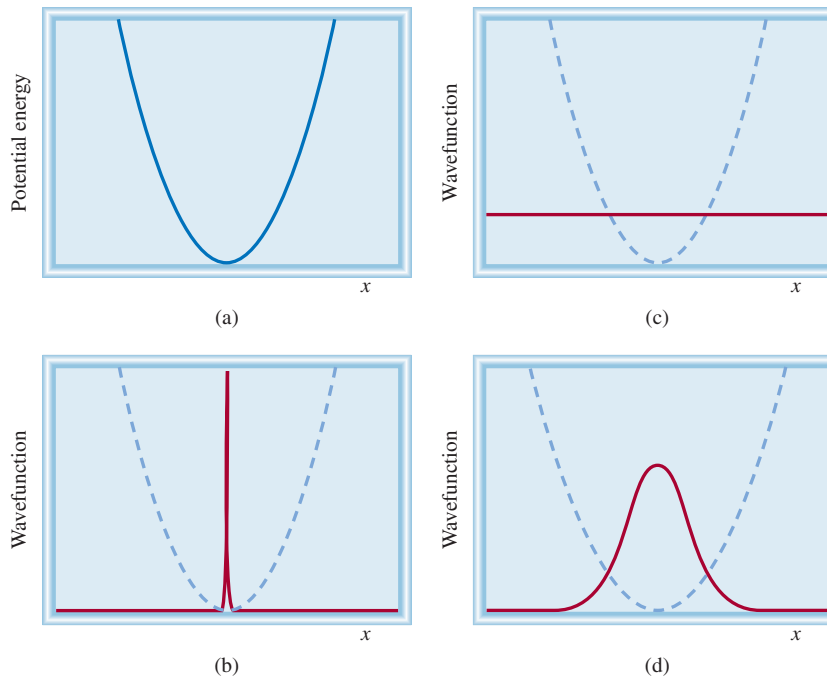**Figure 1.22** (a) A model potential energy function $V(x)$. (b) An example of a ground-state wavefunction that minimizes the potential energy but has a large kinetic energy (high curvature). (c) A ground-state wavefunction that minimizes kinetic energy (low curvature) but has high potential energy (is nonzero in regions where the potential energy is large). (d) The exact ground-state wavefunction.

Figure 1.23 The potential energy for a one-dimensional particle in a box with infinite energy barriers at $x = 0$ and $x = L$.
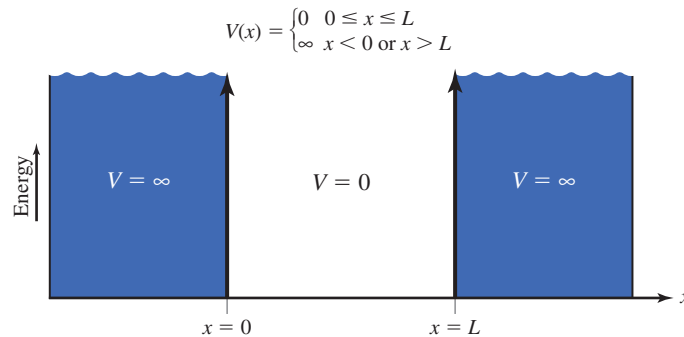
solutions. However, there exist a small number of model systems for which an exact solution is possible. One of these is the particle in a one-dimensional box. Although this system represents a highly idealized situation, the **particle-in-a-box model** possesses many of the features of realistic quantum-mechanical systems, and its solution can be applied to real problems of chemical and biological interest.

Consider a particle of mass m confined to a one-dimensional region (or line) of length L. The potential energy inside the box is zero ($V = 0$) and infinite outside ($V = \infty$). If we denote the position of the particle on the line by x, this potential energy can be written as

$$V(x) = \begin{cases} 0 & 0 \leq x \leq L \\ \infty & x < 0 \text{ or } x > L \end{cases}$$

This potential energy function is shown in Figure 1.23.

Because the potential energy is zero inside the box, the energy of the particle is entirely kinetic. For the region $0 \leq x \leq L$, the Schrödinger equation (Equation 1.24) becomes

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} = E\psi(x)$$

or

$$\frac{d^2\psi(x)}{dx^2} = -\frac{2mE}{\hbar^2} \psi(x) \tag{1.25}$$

The solution to this equation can be obtained because the function we are after yields the original function times a negative constant when it is differentiated twice. The only real functions with this property are the trigonometric functions sine and cosine (see Appendix 1), so a *general* solution is then

$$\psi(x) = A \sin(kx) + B \cos(kx) \tag{1.26}$$

where A, B, and k are constants to be determined. To find the particular solution corresponding to the wavefunction of the particle, we need additional information. Because the probability of finding the particle outside of the box is zero, the wavefunction must also be zero at the boundaries (that is, $\psi(x) = 0$ at $x = 0$ and $x = L$) for the wavefunction to be continuous. (Conditions that specify the value of a function at certain points, such as $\psi(0) = 0$ and $\psi(L) = 0$, are called *boundary conditions.*) Because $\sin(0) = 0$ and $\cos(0) = 1$, Equation 1.26, evaluated at $x = 0$, yields

$$\psi(0) = A \sin(0) + B \cos(0) = 0$$
$$A(0) + B(1) = 0$$

Therefore, $B = 0$, and we have

$$\psi(x) = A\sin(kx)$$

Substituting this expression into Equation 1.25 gives

$$\frac{d^2}{dx^2}\left[A\sin(kx)\right] = -\frac{2mE}{\hbar^2}A\sin(kx)$$

$$-Ak^2\sin(kx) = -\frac{2mE}{\hbar^2}A\sin(kx)$$

Solving for k gives

$$k = \left(\frac{2mE}{\hbar^2}\right)^{1/2}$$

Finally, we have

$$\psi(x) = A\sin\left[\left(\frac{2mE}{\hbar^2}\right)^{1/2}x\right] \tag{1.27}$$

We have yet to use the boundary condition at $x = L$. Requiring $\psi(L) = 0$ in Equation 1.27 gives

$$\psi(L) = A\sin\left[\left(\frac{2mE}{\hbar^2}\right)^{1/2}L\right] = 0 \tag{1.28}$$

One solution to Equation 1.28 is obtained when A is zero; however, this yields a wavefunction that is zero everywhere (that is, it describes a system in which no particle is present), which is trivial, unphysical, and uninteresting. Real, physical solutions are obtained by noting that $\sin(x)$ is zero only when x is a multiple of π (that is, when $x = n\pi$, where n is an integer). Thus, the second boundary condition will be satisfied if the energy E is restricted to values that satisfy[28]

$$\left(\frac{2mE}{\hbar^2}\right)^{1/2}L = n\pi, \quad n = 1, 2, 3, \ldots \tag{1.29}$$

If we define E_n to be the value of E that satisfies Equation 1.29 for a given allowed value of n, we have

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}$$

Using $\hbar = \dfrac{h}{2\pi}$, we have

$$E_n = \frac{n^2h^2}{8mL^2}, \quad n = 1, 2, 3, \ldots \tag{1.30}$$

Because the allowed values of the energy are discrete (not continuous), we say that the energy of this system is *quantized*. This quantization is a direct result of

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28. The value $n = 0$ was excluded because it gives the trivial and unphysical solution that ψ is zero everywhere.

imposing the boundary conditions. In the absence of the confining walls (which generate the boundary conditions), the system describes a *free particle*. The energy of a free particle is not quantized, but can take on any desired positive value. Thus, we see again that quantization of energy arises when a particle (or wave) is confined to a finite region of space.

The difference between successive energy levels can also be calculated from Equation 1.30. For example, the difference between the energy levels n and $(n + 1)$ is

$$\Delta E = E_{n+1} - E_n = \frac{h^2}{8mL^2} \left[(n + 1)^2 - n^2 \right]$$

$$= \frac{h^2}{8mL^2} \left[n^2 + 2n + 1 - n^2 \right]$$

which, after simplification, gives

$$\Delta E_{n \to n+1} = \frac{h^2}{8mL^2} (2n + 1) \tag{1.31}$$

The spacing between successive energy levels is inversely proportional to both the particle mass (m) and L^2, the square of the size of the confining region. The energy-level spacing for this problem also increases with increasing n.

The wavefunctions corresponding to the energy level E_n are

$$\psi_n(x) = A \sin\left(\frac{n\pi x}{L}\right) \tag{1.32}$$

Because $\psi_n^2(x)dx$ represents the probability of finding the particle in the interval defined by x and $x + dx$, the integral of $\psi_n^2(x)$ over all possible values of x must equal 1. Thus, we require that

$$\int_0^L \psi_n^2(x)dx = 1 \tag{1.33}$$

Requiring that the wavefunction given in Equation 1.32 satisfies Equation 1.33 makes it possible to specify the value of A. Substituting Equation 1.32 into Equation 1.33 gives

$$\int_0^L A^2 \sin^2\left(\frac{n\pi x}{L}x\right)dx = 1 \tag{1.34}$$

The integral in Equation 1.34 can be obtained from any decent table of integrals. It equals $L/2$, so $A^2 (L/2) = 1$ or $A = (2/L)^{1/2}$. A wavefunction that satisfies Equation 1.33 is said to be *normalized,* and the preceding process used to find A (the *normalization constant*) is called *normalization.* The properly normalized wavefunctions for the particle in a box are then

$$\psi_n(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) \quad n = 1, 2, 3, \ldots \tag{1.35}$$

The wavefunctions, probability densities [given by $\psi^2(x)$], and energies for the first four energy levels for the particle in a one-dimensional box are plotted in Figure 1.24.
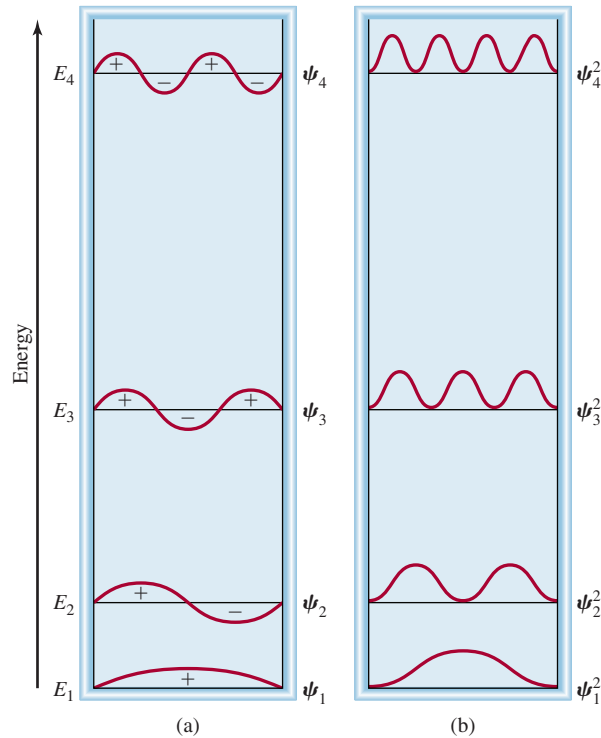
Figure 1.24 Plots of (a) ψ and (b) ψ^2 for the first four energy levels (together with their relative energies) of the particle in a one-dimensional box. The "+" and "−" symbols indicate positive and negative regions of the wavefunction, respectively.

Note that the wavefunctions for the one-dimensional particle in a box look just like the standing waves set up in a vibrating string (Figure 1.17). This similarity is not a coincidence—the mathematics that describes the wave behavior of these two seemingly different physical systems is very similar.

The particle in a one-dimensional box illustrates the following points that are true in general about quantum systems:

▶ The quantization of the energy levels of a system is a direct result of the localization of the particle in a finite region of space by the potential energy. In the particle in a one-dimensional box, the infinite potential energy barriers enforce this localization. In an atom, the negatively charged electrons are confined to a small region around the positively charged nucleus by the strong Coulombic attraction between oppositely charged particles. As a result, their energies are also quantized. For the particle in a one-dimensional box, there is one quantum number *n* that indexes the allowed quantum states. *In general, the number of quantum numbers necessary to describe the quantum state of a particle is equal to the number of dimensions.* For example, the quantum states of a particle in a two-dimensional box require two quantum numbers. We will see in Section 1.4 that the electron in a hydrogen atom, which is an object moving in three dimensions, requires three quantum numbers to specify its wavefunction.

▶ The spacing between successive energy levels is inversely proportional to both the particle mass (*m*) and L^2. For macroscopic objects, both *m* and *L* are large and the resulting spacing between energy levels is vanishingly small, so that the energy spectrum appears continuous, in agreement with the observed classical mechanical behavior of macroscopic objects.

▶ The lowest energy level is not zero. In the particle in a one-dimensional box, the energy of the ground state is $h^2/8mL^2$. This ***zero-point energy*** can be accounted for by the Heisenberg uncertainty principle. If the lowest energy were zero, then the kinetic energy (and thus, the velocity) of the particle would also be zero. There would be no uncertainty in the momentum of the particle; consequently, the uncertainty in the position would be infinite (according to Heisenberg). However, we know that the particle is in the box, so the maximum uncertainty in x is L. As a result, a zero value of the energy would violate the Heisenberg uncertainty principle. The zero-point energy means, too, that the particle can never be at rest because its lowest energy is not zero.

▶ For a given value of n, Equation 1.35 describes the wave behavior of the particle, but the probability density is given by $\psi_n^2(x)$, which is always positive. For $n = 1$, the maximum probability density is at $x = L/2$ (see Figure 1.24); for $n = 2$, the maxima occur at $x = L/4$ and $x = 3L/4$. Generally, the number of nodes (points at which ψ, and hence ψ^2, is zero) increases with increasing energy.

One property of the particle in a box that is not general is the increase in the spacing between successive energy levels with increasing quantum number n. For example, we will see in Section 1.4 that the energy levels in the hydrogen atom become *closer* together for the higher energy levels. In another important model, the *harmonic oscillator,* which is used to describe molecular vibration, the energy-level spacing between successive levels is constant. The dependence of the energy spacing on the quantum number in a one-dimensional problem is a function of the *shape* of the potential energy function.

Example 1.8

Consider an electron confined within a one-dimensional box of length 0.10 nm, which is close to the size of an atom. (a) Calculate the difference in energy between the $n = 2$ and $n = 1$ states of the electron. (b) Repeat the calculation in (a) for a N_2 molecule in a one-dimensional box of length 10.0 cm. (c) Calculate the probability of finding the electron in (a) between $x = 0$ and $x = 0.05$ nm for the $n = 1$ state.

Strategy In (a) and (b) we are interested in the energy difference between two successive energy levels, a quantity described by Equation 1.31. In (c), we are interested in the probability of finding the particle in a given region. To do this we need to find $\psi^2(x)$ and apply Equation 1.23.

Solution (a) Use Equation 1.31 with $n = 1$:

$$\Delta E_{n \to n+1} = \frac{h^2}{8mL^2}(2n + 1)$$

$$= \frac{(6.626 \times 10^{-34} \text{ J/s})^2[2(1) + 1]}{8(9.109 \times 10^{-31} \text{ kg})[(0.10 \text{ nm})(1 \times 10^{-9} \text{ m/nm})]^2}$$

$$= 1.8 \times 10^{-17} \text{ J}$$

This energy difference is similar in magnitude to the difference between the $n = 1$ and $n = 2$ states of the hydrogen atom (see Equation 1.16).

(b) The mass of a single N_2 molecule (m in Equation 1.31) is calculated by dividing the molar mass of nitrogen by Avogadro's number (see Section 0.5), then converting to kg:

$$m(N_2) = \frac{28.02 \text{ g mol}^{-1}}{6.0221 \times 10^{23} \text{ mol}^{-1}} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 4.65 \times 10^{-26} \text{ kg}$$

—Continued

Continued—
Substituting this value into Equation 1.31, and using $L = 10.0$ cm, gives

$$
\begin{aligned}
\Delta E_{n \to n+1} &= \frac{h^2}{8mL^2}(2n + 1) \\
&= \frac{(6.626 \times 10^{-34}\,\text{J/s})^2[2(1) + 1]}{8(4.65 \times 10^{-26}\,\text{kg})[(10.0\,\text{cm})(1 \times 10^{-2}\,\text{m cm}^{-1})]^2} \\
&= 3.5 \times 10^{-40}\,\text{J}
\end{aligned}
$$

This result is 23 orders of magnitude smaller than the energy difference calculated in (a). Compared to the electron, the energy levels of the nitrogen molecule in the box are so closely spaced that they appear almost continuous and would be well approximated by classical mechanics. This is an example of the general rule that quantum mechanical effects become smaller as the size of the confining region increases.

(c) The probability (P) that the electron will be found in the region $0 \leq x \leq L/2$ is given by Equation 1.23 (with $a = 0$ and $b = L/2$):

$$
P = \int_0^{L/2} \psi^2(x)\,dx
$$

Using the normalized wavefunction in Equation 1.35 and setting $n = 1$,

$$
\begin{aligned}
P &= \frac{2}{L}\int_0^{L/2} \sin^2\left(\frac{\pi x}{L}\right)dx \\
&= \frac{2}{L}\left[\frac{x}{2} - \frac{\sin(2\pi x/L)}{4\pi/L}\right]_0^{L/2} \\
&= \frac{1}{2}
\end{aligned}
$$

which is not an unexpected result, classically or quantum mechanically. We could have also done this problem without having to solve the integral by noting that the $n = 1$ probability density is symmetric about $x = L/2$.

Practice Exercise The highest-energy electrons in the molecule butadiene ($H_2C{=}$ $CH{-}CH{=}CH_2$) can be approximated by a particle in a one-dimensional box with a value of L of approximately 580 pm. Calculate the wavelength of light corresponding to an $n = 2$ to $n = 3$ transition in this molecule using the particle-in-a-box model. How does this compare to the experimental value of 217 nm?

Quantum-Mechanical Tunneling

What would happen if the potential walls surrounding the particle in a one-dimensional box were not infinitely high (Figure 1.25)? The particle could escape the box if the kinetic energy of the particle became greater than the potential energy of the walls. What is more surprising, however, is that we might find the particle outside the box even if its kinetic energy is insufficient to reach the top of the barrier! This phenomenon, called *quantum-mechanical tunneling,* has no analog in classical physics. It arises as a consequence of the wave nature of particles. Quantum-mechanical tunneling has many profound consequences in chemistry, physics, and biology.

Figure 1.25 The potential energy for a particle in a one-dimensional box with finite potential walls of height V_0.
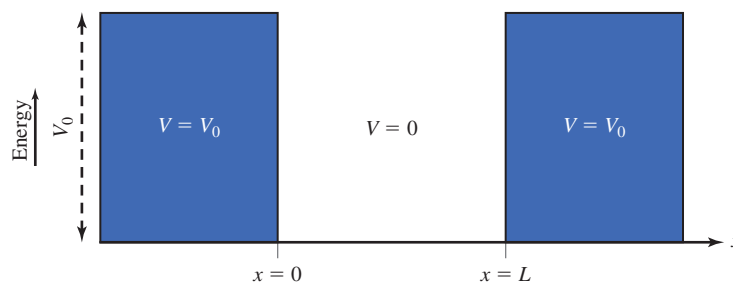
The phenomenon of quantum-mechanical tunneling was introduced in 1928 by the Russian-American physicist George Gamow,[29] and others, to explain α decay, a process in which a nucleus spontaneously decays by emitting an α particle (a helium nucleus, He^{2+}); for example,

$$^{238}_{92}U \longrightarrow \, ^{234}_{90}Th + \alpha$$
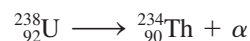
Physicists faced a dilemma: For U-238 decay, the measured kinetic energy of the emitted α particle is about 6×10^{-13} J, whereas the potential barrier to escape from the nucleus is on the order of 4×10^{-11} J, or about 70 times greater than the kinetic energy. How does the α particle overcome the barrier and leave the nucleus? Gamow suggested that the α particle, being a quantum-mechanical object, had wavelike properties that allowed it to penetrate a potential barrier. This explanation turned out to be correct. In general, for finite potential barriers, there is some probability of finding the particle outside the box.

Figure 1.26 illustrates this phenomenon for a particle in a one-dimensional box with finite potential walls. In fact, the probability densities for the ground states for three systems with differing particle masses and barrier heights are shown. In general, the effect of tunneling increases with decreasing particle mass and with decreasing height of the potential barrier.

One important practical application of quantum mechanical tunneling is the scanning tunneling microscope described in the inset on page 109.

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29. Georgy ("George") Antonovich Gamow (1904–1968). Russian-American physicist. In addition to his work on the theoretical nuclear physics, Gamow made important contributions in cosmology and biochemistry.

(a) (b) (c)
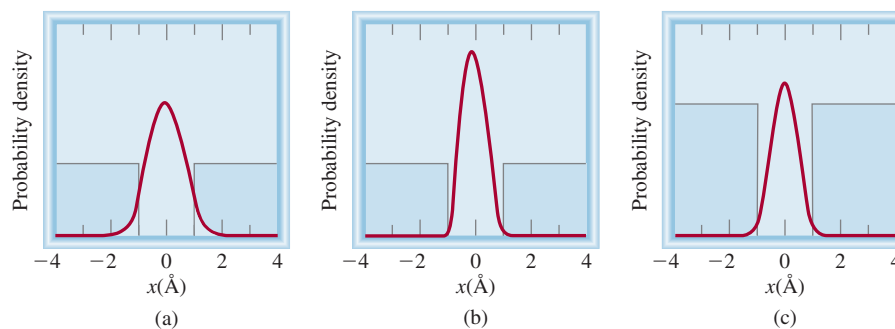
Figure 1.26 Probability densities for the ground state of a particle in a one-dimensional box of length 2 Å with finite potential barriers (as pictured in Figure 1.25). (a) The particle has the mass of an electron and the potential barrier V is equal to the ionization energy of the hydrogen atom. (b) The value of V is the same as in (a), but the mass is that of a hypothetical particle with 10 times the mass of the electron. (c) The particle is an electron, but the potential barrier is twice the hydrogen ionization energy (equal to the ionization energy of He^+). Note that, the total probability outside of the box is significantly less in (b) and (c) than in (a), illustrating that the effect of tunneling is reduced with increasing particle mass and barrier height.

Important Experimental Technique: Electron Microscopy

The electron microscope is an extremely valuable application of the wavelike properties of electrons because it produces images of objects that cannot be seen with the naked eye or with light microscopes. According to the laws of optics, it is impossible to form an image of an object that is smaller than half the wavelength of the light used for the observation. Because the range of visible light wavelengths starts at around 400 nm, or 4×10^{-7} m, we cannot see anything smaller than 2×10^{-7} m. In principle, we can see objects on the atomic and molecular scale by using X-rays, whose wavelengths range from about 0.01 nm to 10 nm. X-rays cannot be focused easily, however, so they do not produce crisp images. Electrons, on the other hand, are charged particles, which can be focused in the same way the image on a TV screen is focused (that is, by applying an electric field or a magnetic field). According to Equation 1.20, the wavelength of an electron is inversely proportional to its velocity. By accelerating electrons to very high velocities, we can obtain wavelengths as short as 0.004 nm.

A different type of electron microscope, called the ***scanning tunneling microscope (STM),*** uses quantum mechanical tunneling to produce an image of the atoms on the surface of a sample. Because of its extremely small mass, an electron is able to move or "tunnel" through an energy barrier (instead of going over it). The STM consists of a metal needle with a very fine point (the source of the tunneling electrons). A voltage is maintained between the needle and the surface of the sample to induce electrons to tunnel through space to the sample. As the needle moves over the sample at a distance of a few atomic diameters from the surface, the tunneling current is measured. This current decreases with increasing distance from the sample. By using a feedback loop, the vertical position of the tip can be adjusted to a constant distance from the surface. The extent of these adjustments, which profile the sample, is recorded and displayed as a three-dimensional false-colored image. Both the electron microscope and the STM are among the most powerful tools in chemical and biological research.

An electron micrograph showing a normal red blood cell and a sickled red blood cell from the same person.
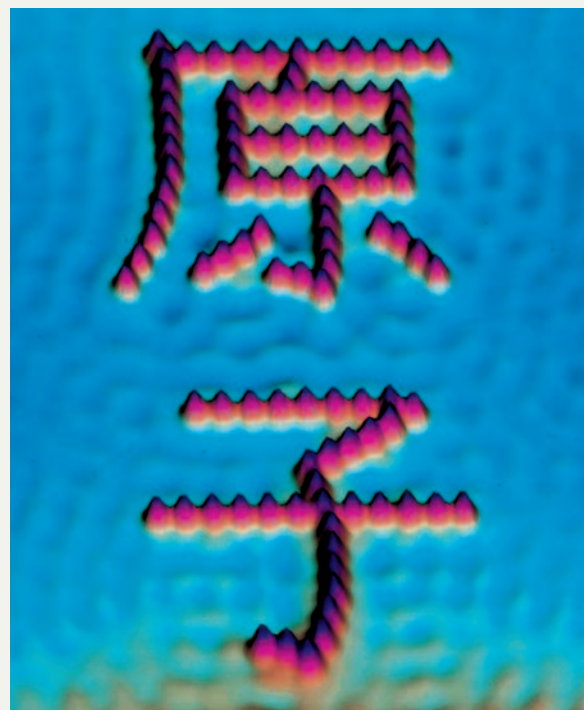
STM image of iron atoms arranged to display the Chinese characters for atom on a copper surface.

1.4 | The Hydrogen Atom Is an Exactly Solvable Quantum-Mechanical System

The simplest atomic system is the hydrogen atom, with its single electron interacting with a positively charged nucleus containing a single proton. Unlike that for the heavier elements, the Schrödinger equation for the electron wavefunctions of a hydrogen atom is exactly solvable. Because the wavefunctions of many-electron atoms

Figure 1.27 The relation between Cartesian coordinates and spherical polar coordinates. For the hydrogen atom, the nucleus is at the origin ($r = 0$), and the electron is at the surface of a sphere of radius r.

$$x = r \sin\theta \cos\phi$$
$$y = r \sin\theta \sin\phi$$
$$z = r \cos\theta$$
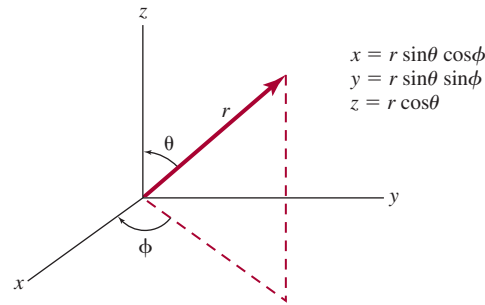
(atoms with more than one electron) share many qualitative properties with those of hydrogen, it is useful to study the hydrogen atom first in some detail.

The Schrödinger Equation for the Hydrogen Atom

By analogy with the one-dimensional Schrödinger equation given in Equation 1.24, the Schrödinger equation for the wavefunction $\psi(x, y, z)$ of a single electron interacting in *three* dimensions with a nucleus of charge $+Ze$ is[30]

$$-\frac{\hbar^2}{2m_e}\left[\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right] + V(x, y, z)\psi = E\psi \tag{1.36}$$

where $V(x, y, z)$ was defined previously in Equation 1.7,

$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

and where $r = \sqrt{x^2 + y^2 + z^2}$ is the distance between the electron and the nucleus. (The symbol ∂ in Equation 1.36 denotes the *partial derivative* and is defined in Appendix 1.)

Because the potential energy depends only on the distance between the nucleus and the electron (that is, it has *spherical symmetry*), Equation 1.36 is most conveniently solved in *spherical polar coordinates*. The relation between Cartesian coordinates (x, y, z) and spherical polar coordinates (r, θ, ϕ) is shown in Figure 1.27. In this coordinate system, the wavefunction is *separable;* that is, it can be written as a product of separate one-dimensional functions of r, θ, and ϕ: $\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$. The exact solution to Equation 1.36 in spherical polar coordinates gives rise to three quantum numbers that index the allowed quantum states. (Remember that the number of quantum numbers is generally equal to the dimensionality of the system. In the particle in a one-dimensional box, for instance, there was only one quantum number.) These quantum numbers and their allowed ranges are

▶ The ***principal quantum number:*** $n = 1, 2, 3, \ldots$
▶ The ***angular momentum quantum number:*** $l = 0, 1, \ldots, n - 1$
▶ The ***magnetic quantum number:*** $m_l = -l, \ldots, -1, 0, 1, \ldots, l$

For each value of n, there are n possible values of l, and for each value of l, there are $2l + 1$ possible values of m_l.

---

30. Actually, because the nucleus is not of infinite mass and is not stationary, the electron mass m_e in Equation 1.36 should be replaced with the *reduced mass* $\mu = m_e m_N/(m_e + m_N)$, where m_e and m_N are the electron and nuclear masses, respectively. However, because $m_e \ll m_N$, the difference between the reduced mass and the electron mass is very small (see Problem 1.60).

Each set of these three quantum numbers (n, l, m_l) represents a valid wavefunction for the electron in a hydrogen atom. The wavefunction for a single electron in an atom is called an ***atomic orbital.*** In quantum mechanics, the position of an electron is described not in terms of orbits, as defined in the Bohr-Sommerfeld model, but in terms of its orbital.

As a result of the spherical symmetry of the potential energy, the energy of the atomic orbitals for hydrogen and hydrogenlike ions depends only upon the value of the principal quantum number (n), and is given by

$$E_n = -\frac{Z^2 e^4 m_e}{8 h^2 \varepsilon_0^2} \frac{1}{n^2} \quad n = 1, 2, 3, \ldots \tag{1.37}$$

which is identical to Equation 1.13, derived using the Bohr model. Note, however, that although the Schrödinger equation for the hydrogen atom is somewhat more complicated than that of the particle in a one-dimensional box, the basic physical origin of the quantization is the same: *Quantization of energy arises when the particle is confined* ("localized") *to a finite region of space*. In the hydrogen atom, the localization of the electron is due to the attractive interaction between the negatively charged electron and the positively charged nucleus.

For $n > 1$, there are multiple orbitals for each value of n, corresponding to different values of l and m_l. Although these combinations of l and m_l represent distinct quantum states of the electron, they have the same energy and are referred to as ***degenerate orbitals.*** (Equation 1.37 shows that the energy depends only on the principal quantum number n.) Collectively, the set of degenerate orbitals at a particular energy is called an ***energy shell.*** For example, the orbitals corresponding to $(n = 2, l = 0, m_l = 0)$ and $(n = 2, l = 1, m_l = -1)$ are degenerate and are both members of the second $(n = 2)$ energy shell of the hydrogen atom. Within a given energy shell, a set of distinct orbitals that all possess the same value of l form a ***subshell.*** The subshells are generally designated by the letters $s, p, d, \ldots$, as follows:

l	0	1	2	3	4	5
Name of Subshell	s	p	d	f	g	h

Thus, the set of orbitals with $n = 2$ and $l = 1$ is referred to as a $2p$ subshell and its three orbitals (corresponding to $m_1 = -1$, 0, and $+1$, respectively) are called the $2p$ orbitals. The unusual sequence of letters (s, p, and d) has an historical origin that predates quantum mechanics. Physicists who studied atomic emission spectra tried to correlate the observed spectral lines with the particular quantum states involved in the transitions. They noted that some of the lines were ***s***harp; some were rather spread out, or ***d***iffuse; and some were very strong and hence were referred to as ***p***rincipal lines. Subsequently, the initial letters of each adjective were assigned to the quantum states. However, after the letter d and starting with the letter f (for ***f***undamental), the orbital designations follow alphabetical order.

Hydrogenlike Atomic Orbitals

The electron wavefunctions (or atomic orbitals) for the hydrogen atom (and hydrogenlike ions, such as He^+, Li^{2+}, and so on) are given by

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)\, Y_{lm_l}(\theta, \phi) \tag{1.38}$$

where $R_{nl}(r)$ is the radial (r dependent) part of the wavefunction and the angular func-
tions $Y_{lm_l}(\theta, \phi)$ are called *spherical harmonics.*[31] These radial and angular functions
for the first three energy shells are shown in Tables 1.2 and 1.3, respectively. A specific

Table 1.2	Radial Part of Hydrogenlike Atomic Orbitals[†]		
n	**l**	**Orbital Name**	$R_{nl}(\bar{r}); \ \bar{r} \equiv Zr/a_0$
1	0	$1s$	$2\left(\dfrac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\bar{r}}$
2	0	$2s$	$\dfrac{\sqrt{2}}{4}\left(\dfrac{Z}{a_0}\right)^{\frac{3}{2}}(2 - \bar{r})e^{-\bar{r}/2}$
	1	$2p$	$\dfrac{\sqrt{6}}{12}\left(\dfrac{Z}{a_0}\right)^{\frac{3}{2}}\bar{r}e^{-\bar{r}/2}$
3	0	$3s$	$\dfrac{2\sqrt{3}}{243}\left(\dfrac{Z}{a_0}\right)^{\frac{3}{2}}(27 - 18\bar{r} + 2\bar{r}^2)e^{-\bar{r}/3}$
	1	$3p$	$\dfrac{2\sqrt{6}}{243}\left(\dfrac{Z}{a_0}\right)^{\frac{3}{2}}(6\bar{r} - \bar{r}^2)e^{-\bar{r}/3}$
	2	$3d$	$\dfrac{4\sqrt{30}}{2430}\left(\dfrac{Z}{a_0}\right)^{\frac{3}{2}}\bar{r}^2 e^{-\bar{r}/3}$

[†]a_0 is the Bohr radius (see section 1.2).

Table 1.3	Angular Part of Hydrogenlike Atomic Orbitals		
l	**m_l**	**Suborbital Name**	$Y_{lm_l}(\theta, \phi)$*
0	0	s	$\left(\dfrac{1}{4\pi}\right)^{\frac{1}{2}}$
1	0	p_z	$\left(\dfrac{3}{4\pi}\right)^{\frac{1}{2}}\cos\theta$
	± 1	p_x	$\left(\dfrac{3}{4\pi}\right)^{\frac{1}{2}}\sin\theta\cos\phi$
	± 1	p_y	$\left(\dfrac{3}{4\pi}\right)^{\frac{1}{2}}\sin\theta\sin\phi$
2	0	d_{z^2}	$\left(\dfrac{15}{16\pi}\right)^{\frac{1}{2}}[3\cos^2\theta - 1]$
	± 1	d_{xz}	$\left(\dfrac{15}{16\pi}\right)^{\frac{1}{2}}\sin\theta\cos\theta\cos\phi$
	± 1	d_{yz}	$\left(\dfrac{15}{16\pi}\right)^{\frac{1}{2}}\sin\theta\cos\theta\sin\phi$
	± 2	d_{xy}	$\left(\dfrac{15}{16\pi}\right)^{\frac{1}{2}}\sin^2\theta\sin 2\phi$
	± 2	$d_{x^2-y^2}$	$\left(\dfrac{15}{16\pi}\right)^{\frac{1}{2}}\sin^2\theta\cos 2\phi$

*For $m_l > 0$, the orbitals shown here are the real orbitals constructed by combining the complex orbitals corresponding
to $+m_l$ and $-m_l$.

31. The spherical harmonics can be written as a product of a function of θ and a function of
ϕ: $Y_{lm_l}(\theta,\phi) = S_{lm_l}(\theta)\Phi_m(\phi)$, so the wavefunction in Equation 1.38 is separable.

orbital (n, l, m_l) is constructed by multiplying the radial factor $R_{nl}(r)$ in Table 1.2 by the angular function $Y_{lm_l}(\theta, \phi)$ in Table 1.3.

The actual orbitals with $m_l \geq 1$ are complex, making visualization inconvenient. However, because they are equal in energy, the orbitals with $+m_l$ and $-m_l$ within a given subshell can be combined to form two alternate orbitals that are entirely real. It is the real orbitals that are given in Table 1.3. For $n = 2$, for example, the two complex orbitals with $l = 1$ and $m_l = \pm 1$, are

$$\psi_{2,1,1}(r, \theta, \phi) = \left(\frac{3}{8\pi}\right)^{1/2} R_{21}(r)\cos(\theta)e^{+i\phi}$$

$$\psi_{2,1,-1}(r, \theta, \phi) = \left(\frac{3}{8\pi}\right)^{1/2} R_{21}(r)\cos(\theta)e^{-i\phi}$$

where $i = \sqrt{-1}$ and the complex exponentials are given by $e^{i\phi} = \cos(\phi) + i\sin(\phi)$ and $e^{-i\phi} = \cos(\phi) - i\sin(\phi)$. Adding and subtracting these two complex orbitals gives the real $2p_x$ and $2p_y$ orbitals:

$$\psi(2p_x) = \frac{1}{\sqrt{2}}[\psi_{2,1,1} + \psi_{2,1,-1}] = \left(\frac{1}{\sqrt{2}}\right)\left(\frac{3}{8\pi}\right)^{1/2} R_{21}(r)\cos(\theta)[e^{i\phi} + e^{-i\phi}]$$

$$= \left(\frac{3}{4\pi}\right)^{1/2} R_{21}(r)\cos(\theta)\cos(\phi) \tag{1.39}$$

$$\psi(2p_y) = \frac{1}{\sqrt{2}}[\psi_{2,1,1} - \psi_{2,1,-1}] = \left(\frac{1}{\sqrt{2}}\right)\left(\frac{3}{8\pi}\right)^{1/2} R_{21}(r)\cos(\theta)[e^{i\phi} - e^{-i\phi}]$$

$$= \left(\frac{3}{4\pi}\right)^{1/2} R_{21}(r)\cos(\theta)\sin(\phi) \tag{1.40}$$

(The factor $1/\sqrt{2}$ is included to ensure proper normalization.) The $2p_z$ orbital corresponds directly to the orbital with $(n = 2, l = 1, m_l = 0)$, which is real.

Table 1.4 summarizes the relationship between quantum numbers and hydrogen-like atomic orbitals. When $l = 0$, $(2l + 1) = 1$ and there is only one value of m_l, so we have an s orbital. When $l = 1$, $(2l + 1) = 3$, so there are three values of m_l, giving rise to three p orbitals, labeled p_x, p_y, and p_z. When $l = 2$, $(2l + 1) = 5$, so there are five values of m_l, and the corresponding five d orbitals are labeled with more elaborate subscripts. In the following sections we discuss the s, p, and d orbitals separately.

Table 1.4	Relationship between Quantum Numbers and Atomic Orbitals			
n	**l**	**m_l**	**Number of Orbitals**	**Atomic Orbital Designations**
1	0	0	1	$1s$
2	0	0	1	$2s$
	1	−1, 0, 1	3	$2p_x$, $2p_y$, $2p_z$
3	0	0	1	$3s$
	1	−1, 0, 1	3	$3p_x$, $3p_y$, $3p_z$
	2	−2, −1, 0, 1, 2	5	$3d_{xy}$, $3d_{yz}$, $3d_{xz}$, $3d_{x^2-y^2}$, $3d_{z^2}$

Figure 1.28 (a) A useful measure of the electron density in a 1s orbital is obtained by first dividing the orbital into successive thin spherical shells of thickness *dr*. (b) A plot of the probability of finding a 1s electron in each shell, called the radial probability function, as a function of distance from the nucleus shows a maximum at 52.9 pm from the nucleus. Interestingly, this is equal to the Bohr radius.
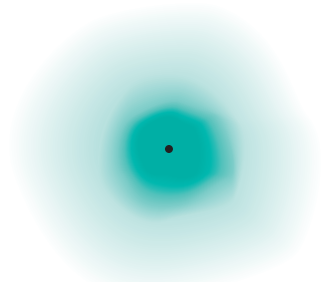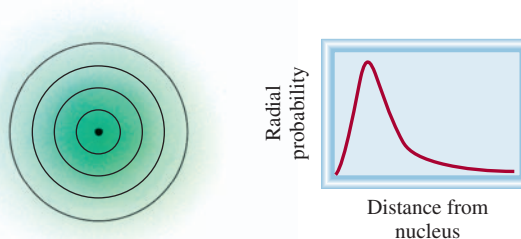
A representation of the electron density distribution surrounding the nucleus in the hydrogen atom. It shows a high probability of finding the electron closer to the nucleus.

s Orbitals

What are the shapes of the orbitals? Strictly speaking, an orbital does not have a well-defined shape because the wavefunction characterizing the orbital extends from the nucleus to infinity. In that sense, it is difficult to say what an orbital looks like. On the other hand, it is convenient to think of orbitals as having specific shapes, particularly when discussing the formation of chemical bonds between atoms, as we will do in Chapters 3 and 4.

According to Table 1.3, an *s* orbital, defined as any atomic orbital with $l = 0$, has no dependence on θ or ϕ. It depends only on *r*. Such a function is said to be *spherically symmetric* and is defined by the radial function $R_{n0}(r)$. To get a sense of where the electrons are likely to be in these orbitals, we plot the probability of finding the electron in a spherical shell of thickness *dr* at a distance of *r* from the nucleus (see Figure 1.27). This probability, denoted by $P(r)$, is given by the expression

$$P(r) = r^2 [R(r)]^2 \tag{1.41}$$

which is called the **radial probability function**. (The factor r^2 in Equation 1.41 comes from the fact that the surface area of the sphere[32] of radius *r* increases as r^2.) Figure 1.28 illustrates the radial probability function for the 1s orbital.

The wavefunctions and radial distribution functions for the 1s, 2s, and 3s hydrogenlike atomic orbitals are shown in Figure 1.29 as functions of *r*. Note that the wavefunctions for the 1s, 2s, and 3s orbitals have 0, 1, and 2 *nodes* (points where the wavefunction is zero), respectively. For a general *s* orbital with principal quantum number *n*, the number of nodes is $n - 1$. This increase in the number of nodes as the energy of the particle increases was also seen in the particle in a one-dimensional box and is a general feature of quantum systems.

Also shown in Figure 1.29(c) for the 1s, 2s, and 3s orbitals are the corresponding **boundary surface diagrams,** defined as a surface containing 90 percent of the total electron density (defined as ψ^2) in the orbital. The boundary surface diagram serves as a useful representation of the shape of the orbital. All *s* orbitals are spherical but differ in size, which increases as the principal quantum number increases.

p Orbitals

The *p* orbitals come into existence starting with the principal quantum number $n = 2$. If $n = 1$, then the angular momentum quantum number can only assume the value of zero; therefore, there are no 1p orbitals, just a 1s orbital. As we saw earlier, the magnetic quantum number m_l can have values of -1, 0, and 1 when $l = 1$. Starting with

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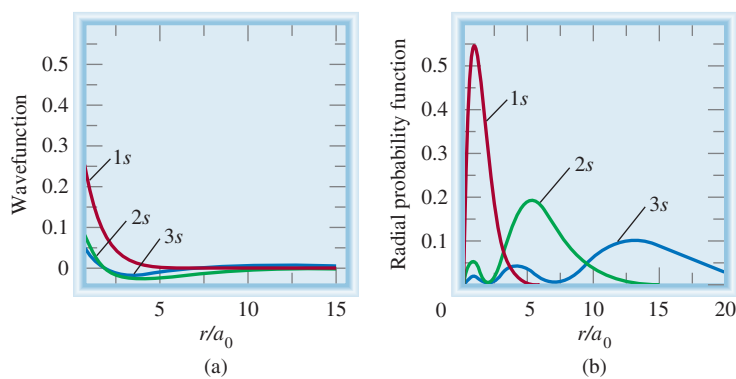
32. The surface area of a sphere of radius *r* is $4\pi r^2$.

Figure 1.29 (a) The wavefunctions for the 1*s*, 2*s*, and 3*s* orbitals plotted as functions of *r* in units of the Bohr radius, $a_0 =$ 52.9 pm (see Example 1.4). (b) The radial probability functions for the same orbitals. (c) The 90% boundary surfaces for the orbitals in (a). The radii of the boundary surfaces are 2.65 a_0, 9.20 a_0, and 19.5 a_0, for the 1*s*, 2*s* and 3*s* orbitals, respectively. Roughly speaking the size of an orbital is proportional to n^2, where *n* is the principal quantum number.
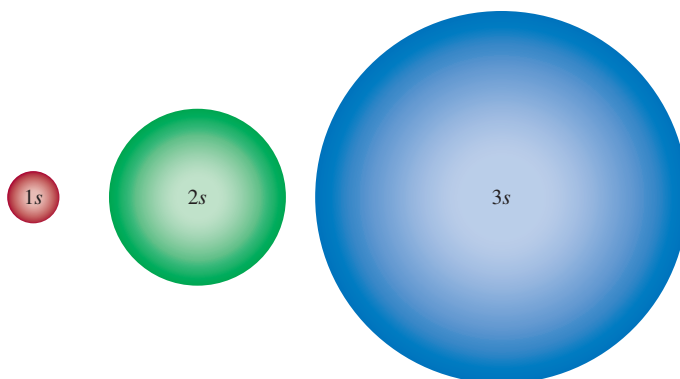
n = 2 and *l* = 1, the three values of m_l correspond to the three 2*p* orbitals: $2p_x$, $2p_y$, and $2p_z$. The shapes of orbitals are determined by the angular parts of the wavefunction given in Table 1.3 and Equations 1.39 and 1.40. For *p* orbitals, the angular part depends on θ and ϕ, so the *p* orbitals are not spherically symmetric. The letter subscripts *x*, *y*, and *z* in the orbital name indicate the axes along which the orbitals are oriented. The "dumbbell" shape of the three *p* orbitals is represented in Figure 1.30, where the "+" and "−" signs on the orbital lobes indicate the sign of the wavefunction.

For the wavefunction to change sign, it must go through zero. Each *p* orbital has a *nodal plane,* defined as a *plane in which the wavefunction is zero,* in the plane perpendicular to the orientation axis. For example, the *y-z* plane (where *x* = 0) is the nodal plane for the p_x orbital. The three *p* orbitals are identical in size, shape, and energy; they differ from one another only in orientation. The radial parts of the
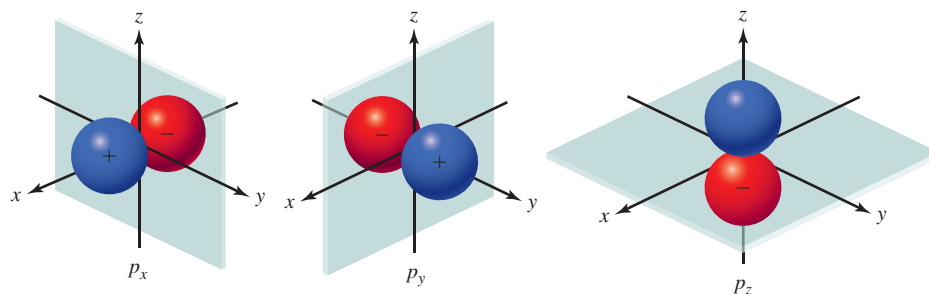

Figure 1.30 The shapes of the three *p* orbitals showing the sign of the wavefunction and the nodal planes.
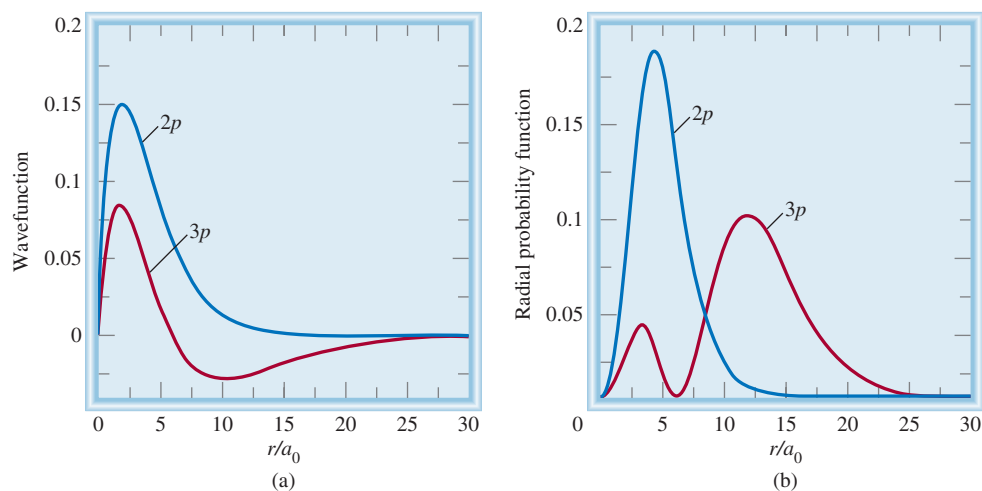
Figure 1.31 (a) The radial part of the wavefunction for the $2p$ and $3p$ hydrogen atomic orbitals. (b) The radial probability function for the orbitals shown in (a).

wavefunctions for the $2p$ and $3p$ orbitals are shown in Figure 1.31, together with the corresponding radial probability functions.[33] Like s orbitals, p orbitals increase in size with increasing principal quantum number n.

d Orbitals and Beyond

When $l = 2$, there are five values of m_l (-2, -1, 0, 1, and 2), which correspond to five d orbitals. The lowest value of n for a d orbital is 3. When $n = 3$ and $l = 2$, we have five $3d$ orbitals, which in their real representations are denoted $3d_{xy}$, $3d_{xz}$, $3d_{yz}$, $3d_{x^2-y^2}$, and $3d_{z^2}$ (the subscripts contain information about their shape and orientation). Representations of the various $3d$ orbitals indicating the shape, sign, and nodal planes are shown in Figure 1.32. Each d orbital has two nodal planes. All the $3d$ orbitals in a hydrogen atom are identical in energy. The d orbitals corresponding to n greater than 3 ($4d$, $5d$, . . .) have similar shapes but are more extended in space (that is, they are larger).

Orbitals with l greater than 2 are labeled f, g, and so on. The f orbitals ($l = 3$) are important in accounting for the behavior of elements with atomic numbers greater than 57, but their shapes are difficult to represent. In general chemistry we are not concerned with orbitals having l values greater than 3 (the g orbitals and beyond).

Example 1.9

List the values of n, l, and ml for orbitals in the $4d$ subshell.

Strategy Use the relationships between n, l, and m_l to solve this problem. What, for example, do the "4" and "d" represent in $4d$?

—Continued

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33. From Figure 1.31 you can see that the radial part of the $3p$ orbital has one node, whereas that for $2p$ has no nodes. Nodes in the radial part of the wavefunction are called *radial nodes*. For the hydrogen atom, the number of radial nodes is equal to $(n - l - 1)$. The nodal planes, for which a p orbital has one and an s orbital has none, are called *angular nodes*. The number of angular nodes is equal to l. The total number of nodes in a hydrogen atom orbital (angular + radial) is then given by $(n - l - 1) + l = n - 1$.
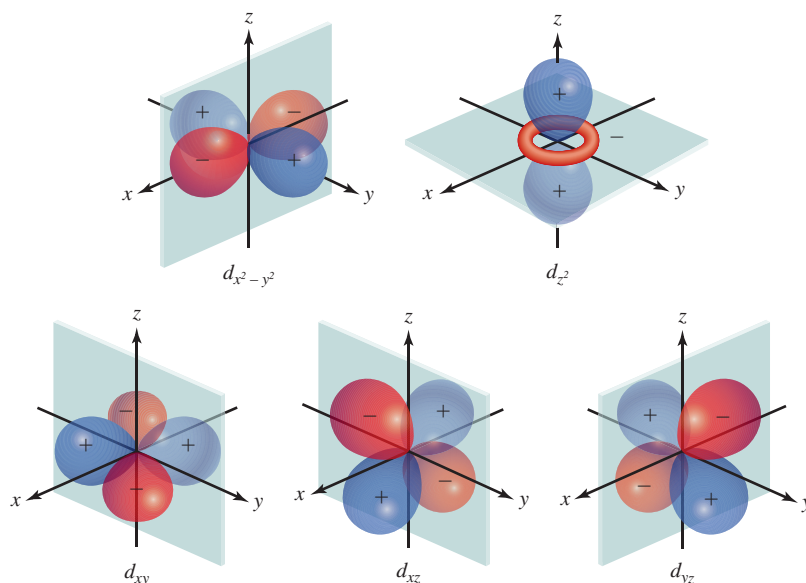
Figure 1.32 The shapes of the five *d* orbitals showing the sign of the wavefunction and the nodal surfaces.

Continued—

Solution The number given in the designation of the subshell is the principal quantum number, so in this case $n = 4$. The letter designates the type of orbital. Because we are dealing with *d* orbitals, $l = 2$. The values of m_l can vary from $-l$ to $+l$ (that is, from -2 to 2). Therefore, m_l can be -2, -1, 0, 1, or 2.

Check The values of *n* and *l* are fixed for 4*d*, but m_l can have any one of the five values that correspond to the five *d* orbitals.

Practice Exercise Give the values of the quantum numbers associated with the orbitals in the 5*f* subshell.

Electron Spin and the Electron Spin Quantum Number (m_s)

Experiments on the emission spectra of hydrogen and sodium atoms indicated that lines in the emission spectra could be split by the application of an external magnetic field. In 1925 Samuel Goudsmit[34] and George Uhlenbeck[35] postulated that these magnetic properties could be explained if electrons possessed an intrinsic angular momentum—as if they were spinning on their own axes, as Earth does. According to electromagnetic theory, a spinning charge generates a magnetic field, and it is this motion that causes an electron to behave like a magnet. These electron magnets are

34. Samuel Abraham Goudsmit (1902–1978). Dutch-American physicist. While a student of Paul Ehrenfest at the University of Leiden in 1925, he and fellow student George Uhlenbeck postulated the existence of intrinsic electron spin. Goudsmit was the scientific leader of Operation Alsos at the end of World War II, whose mission was to determine the progress of German efforts toward an atomic bomb.

35. George Eugène Uhlenbeck (1900–1988). Dutch-American physicist. Born in Indonesia (then a Dutch colony), Uhlenbeck studied at the University of Leiden with Paul Ehrenfest, where he, with fellow student Samuel Goudsmit, postulated the existence of intrinsic electron spin. In addition to his work on quantum mechanics, Uhlenbeck made fundamental advances in statistical mechanics and the theory of random processes.
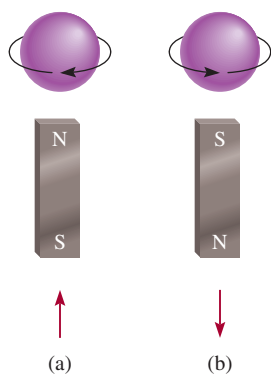
Figure 1.33 The (a) clockwise and (b) counterclockwise spins of an electron. The magnetic fields generated by these two spinning motions are analogous to those from the two magnets. The upward and downward arrows are used to denote the direction of "spin."

highly quantum mechanical and are quantized so that only two possible spinning motions of an electron are possible, clockwise and counterclockwise (Figure 1.33). To take this *electron spin* into account, it is necessary to introduce a fourth quantum number, the *electron spin quantum number* (m_s), which has a value of $+\frac{1}{2}$ or $-\frac{1}{2}$. It is customary to refer to a value $m_s = +\frac{1}{2}$ as "spin up" and to a value $m_s = -\frac{1}{2}$ as "spin down."

One major piece of evidence that led Goudsmit and Uhlenbeck to postulate the existence of electron spin came from an experiment performed by Otto Stern[36] and Walther Gerlach[37] in 1922. Figure 1.34 shows their basic experimental arrangement. In such an experiment, a beam of gaseous hydrogen atoms generated in a hot furnace passes through a nonhomogeneous magnetic field. The interaction between this electron in each atom and the magnetic field causes the atom to be deflected from its straight-line path. Because the spin of each electron can be either "up" or "down," with equal probability, one half of the atoms are deflected in one way; and the other half of the atoms are deflected in the other direction. Thus, two spots of equal intensity are observed on the detecting screen.

It must be noted that the picture of the electron as a tiny spinning magnet, although useful and convenient as a visualization tool, should not be taken literally. On a fundamental level, the electron "spin" can only be understood by going beyond the Schrödinger equation to include the effects of Einstein's theory of special relativity.

To summarize, the quantum state of an electron in hydrogen (or a hydrogenlike ion) is *completely* specified by the four quantum numbers n, l, m_l, and m_s. The energy of this electron is determined only by the value of the *principal quantum number n* (according to Equation 1.37). The *angular momentum quantum number l* determines the basic shape of the orbital, and the *magnetic quantum number m_l* determines its orientation in space. The *electron spin quantum number m_s* determines the intrinsic "spin" of the electron. We will see in Chapter 2 that although an exact solution to the

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36. Otto Stern (1888–1969). German physicist. He made important contributions to the study of the magnetic properties of atoms and to the kinetic theory of gases. Stern was awarded the Nobel Prize in Physics in 1943.

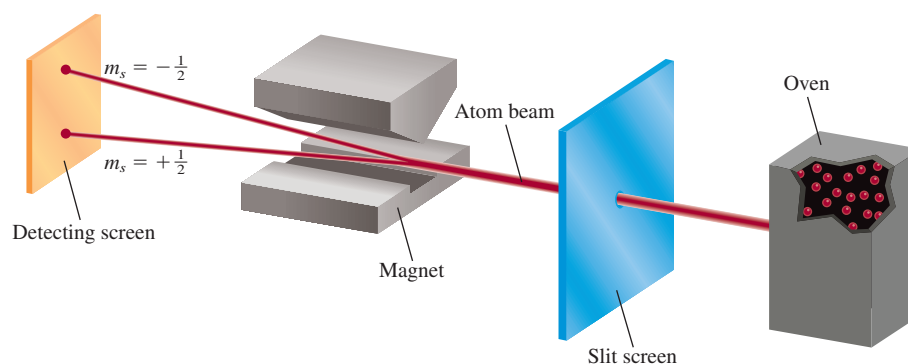37. Walther Gerlach (1889–1979). German physicist. Gerlach's main area of research was in quantum theory.

Figure 1.34 Experimental arrangement for demonstrating the existence of electron spin. A beam of atoms is directed through a magnetic field. When a hydrogen atom with a single electron passes through the field, it is deflected in one direction or the other, depending on the direction of the spin of its electron. In a stream consisting of many atoms, there will be equal distribution of the two kinds of spins, so that two spots of equal intensity are detected on the screen.

Schrödinger equation for many-electron atoms is not possible, the four hydrogen quantum numbers, and the basic orbital shapes they represent, retain their usefulness in describing the quantum state of the electrons in those atoms. *Most importantly, the mathematical properties of these four quantum numbers form the basis for the buildup of the elements in the periodic table.*

Summary of Facts and Concepts

Section 1.1

▸ At the end of the nineteenth century, scientists began to realize that the laws of classical physics were incompatible with a number of new experiments that probed the nature of atoms and molecules and their interaction with light. Through the work of a number of scientists over the first three decades of the twentieth century, a new theory—quantum mechanics—was developed that was able to explain the behavior of objects on the atomic and molecular scale.

▸ The quantum theory developed by Planck successfully explains the emission of radiation by heated solids. The quantum theory states that radiant energy is emitted by atoms and molecules in small discrete amounts (quanta), rather than over a continuous range. This behavior is governed by the relationship $E = h\nu$, where E is the energy of the radiation, h is Planck's constant, and ν is the frequency of the radiation. Energy is always emitted in whole-number multiples of $h\nu$ ($1\ h\nu$, $2\ h\nu$, $3\ h\nu$, . . .).

▸ Using quantum theory, Einstein solved another mystery of physics—the photoelectric effect. Einstein proposed that light can behave like a stream of particles (photons).

Section 1.2

▸ The line spectrum of hydrogen, yet another mystery to nineteenth-century physicists, was also explained by applying an early version of quantum theory. Bohr developed a model of the hydrogen atom in which the energy of its single electron is quantized, limited to certain energy values determined by an integer called the quantum number.

▸ The lowest energy state of an electron is its ground state, and states with energies higher than the ground-state energy are excited states. In the Bohr model, an electron emits a photon when it drops from a higher-energy state to a lower-energy state. The release of specific amounts of energy in the form of photons accounts for the lines in the hydrogen emission spectrum.

▸ In spite of its success with the hydrogen atom, the Bohr model was deficient because it was unable to account for the emission spectra of heavier atoms, such as helium.

Section 1.3

▸ De Broglie extended Einstein's wave-particle description of light to all matter in motion. The wavelength of a moving particle of mass m and velocity u is given by the de Broglie equation $\lambda = h/mu$ (Equation 1.20).

▸ The realization that matter at the atomic and subatomic scale possesses wavelike properties lead to the development of the Heisenberg uncertainty principle, which states that it is impossible to know simultaneously both the position (x) and the momentum (p) of a particle with certainty (see Equation 1.22).

▸ The Schrödinger equation (Equation 1.24) describes the motions and energies of submicroscopic particles. This equation, in which the state of a quantum particle is described by its wavefunction, launched modern quantum mechanics and a new era in physics. The wavefunction contains information about the probability of finding a particle in a given region of space.

▸ The Schrödinger equation can be exactly solved for a "particle in a one-dimentional box," an idealized model, which, despite its simplicity, can be applied to understand the behavior of a number of real systems of chemical and biological interest.

▸ Because of the wave nature of matter, a quantum particle can sometimes overcome energy barriers that the particle, if behaving classically, would have insufficient energy to cross. This phenomenon, called quantum tunneling, is the basis for a number of scientific applications, such as the scanning tunneling microscope (STM).

Section 1.4

▸ The Schrödinger equation tells us the possible energy states of the electron in a hydrogen atom and the probability of its location in a particular region surrounding the nucleus.

▸ The quantum state of an electron in a hydrogen atom is given by its wavefunction (or atomic orbital) [$\psi(r, \theta, \phi)$] and the distribution of electron density in space is given by $\psi^2(r, \theta, \phi)$. The sizes and shapes of atomic orbitals can be represented by electron density diagrams or boundary surface diagrams.

▸ Four quantum numbers characterize the electron wavefunction (atomic orbital) in a hydrogen atom: The principal quantum number n identifies the main energy level, or shell, of the orbital; the angular momentum quantum number l indicates the shape of the orbital; the magnetic quantum number m_l specifies the orientation of the orbital in space; and the electron spin quantum

number m_s indicates the direction of the electron's spin on its own axis.

▶ The single s orbital for each energy level is spherical and centered on the nucleus. There are three p orbitals present at $n = 2$ and higher; each has two lobes, and the pairs of lobes are arranged at right angles to one another. Starting with $n = 3$, there are five d orbitals, with more complex shapes and orientations.

▶ The energy of the electron in a hydrogen atom is determined solely by its principal quantum number.

Key Words

Problems

Classical Physics Does Not Adequately Describe the Interaction of Light with Matter

1.1 (a) What is the wavelength (in nanometers) of light having a frequency of 8.6×10^{13} Hz? (b) What is the frequency (in Hz) of light having a wavelength of 566 nm?

1.2 (a) What is the frequency of light having a wavelength of 456 nm? (b) What is the wavelength (in nanometers) of radiation having a frequency of 2.45×10^9 Hz? (This is the type of radiation used in microwave ovens.)

1.3 The SI unit of time is the second, which is defined as 9,192,631,770 cycles of radiation associated with a certain emission process in the cesium atom. Calculate the wavelength of this radiation (to three significant figures). In which region of the electromagnetic spectrum is this wavelength found?

1.4 The SI unit of length is the meter, which is defined as the length equal to 1,650,763.73 wavelengths of the light emitted by a particular energy transition in krypton atoms. Calculate the frequency of the light to three significant figures.

1.5 A photon has a wavelength of 624 nm. Calculate the energy of the photon in joules.

1.6 The blue of the sky results from the scattering of sunlight by air molecules. The blue light has a frequency of about 7.5×10^{14} Hz. (a) Calculate the wavelength, in nm, associated with this radiation, and (b) calculate the energy, in joules, of a single photon associated with this frequency.

1.7 A photon has a frequency of 6.0×10^4 Hz. (a) Convert this frequency into wavelength (nm). Into what region of the electromagnetic spectrum does this frequency fall? (b) Calculate the energy (in joules) of this photon. (c) Calculate the energy (in joules) of 1 mol of photons all with this frequency.

1.8 What is the wavelength, in nm, of radiation that has an energy content of 1.0×10^3 kJ mol^{-1}? In which region of the electromagnetic spectrum is this radiation found?

1.9 When copper is bombarded with high-energy electrons, X-rays are emitted. Calculate the energy (in joules) associated with the photons if the wavelength of the X-rays is 0.154 nm.

1.10 A particular form of electromagnetic radiation has a frequency of 8.11×10^{14} Hz. (a) What is its wavelength in nanometers? In meters? (b) To what region of the electromagnetic spectrum would you assign it? (c) What is the energy (in joules) of one quantum of this radiation?

1.11 The retina of the human eye can detect light when the radiant energy incident on it exceeds a minimum value of 4.0×10^{-17} J. How many photons does this energy correspond to if the light has a wavelength of 600 nm?

1.12 A microwave oven operating at a wavelength of 1.22×10^8 nm is used to heat 150 mL of water (roughly the volume of a tea cup) from 20°C to 100°C. Given that it takes 4.186 J of energy to heat 1 mL of water by 1°C, calculate the number of photons needed if 92.0 percent of the microwave energy is converted into the thermal energy of water.

1.13 Careful spectral analysis shows that the familiar yellow light of sodium vapor lamps (used in some streetlights) is made up of photons of two wavelengths, 589.0 nm and 589.6 nm. What is the difference in energy (in joules) between photons with these wavelengths?

1.14 Explain how scientists are able to measure the temperature of the surface of stars. (*Hint:* Treat stellar radiation like radiation from a blackbody.)

1.15 Using Wien's law, calculate the temperatures for which the values of λ_{max} for blackbody radiation are 100 nm, 300 nm, 500 nm, and 800 nm. To what region of the electromagnetic spectrum does each of these wavelengths correspond? Using your results, speculate as to how night vision goggles might work.

1.16 A photoelectric experiment was performed by separately shining a laser at 450 nm (blue light) and a laser at 560 nm (yellow light) on a clean metal surface and measuring the number and kinetic energy of the ejected electrons. Which light would generate more electrons? Which light would eject electrons with the greatest kinetic energy? Assume that the same number of photons is delivered to the metal surface by each laser and that the frequencies of the laser lights exceed the threshold frequency.

1.17 In a photoelectric experiment, a student uses a light source whose frequency is greater than that needed to eject electrons from a certain metal. However, after continuously shining the light on the same area of the metal for a long period, the student notices that the maximum kinetic energy of ejected electrons begins to decrease, even though the frequency of the light is held constant. How would you account for this behavior?

1.18 The maximum wavelength of light that can be used to eject electrons from a clean sodium metal surface is 520 nm. (a) Calculate the photoelectric work function (in joules) for sodium. (b) If 450-nm light is used, what is the kinetic energy of the ejected electrons?

1.19 The threshold frequency for dislodging an electron from a clean zinc metal surface is 8.54×10^{14} Hz. Calculate the minimum amount of energy (in joules) required to remove an electron from the zinc surface (that is, calculate the work function for zinc).

The Bohr Model Was an Early Attempt to Formulate a Quantum Theory of Matter

1.20 Some copper compounds emit green light when they are heated in a flame. How would you determine whether the light is of one wavelength or a mixture of two or more wavelengths?

1.21 How is it possible for a fluorescent material to emit radiation in the ultraviolet region after absorbing visible light. Explain your answer.

1.22 Explain how astronomers are able to tell which elements are present in distant stars by analyzing the electromagnetic radiation emitted by the stars.

1.23 Consider the following energy levels of a hypothetical atom:

E_4: -1.0×10^{-19} J

E_3: -5.0×10^{-19} J

E_2: -10×10^{-19} J

E_1: -15×10^{-19} J

(a) What is the wavelength of the photon needed to excite an electron from E_1 to E_4? (b) What is the energy (in joules) a photon must have to excite an electron from E_2 to E_3? (c) When an electron drops from the E_3 level to the E_1 level, the atom is said to undergo emission. Calculate the wavelength of the photon emitted in this process.

1.24 The first line of the Balmer series occurs at a wavelength of 656.3 nm. What is the energy difference between the two energy levels involved in the emission that results in this spectral line?

1.25 Calculate the wavelength (in nm) of a photon that must be absorbed by the electron in a hydrogen atom to excite it from the $n = 3$ to the $n = 5$ energy level.

1.26 Calculate the frequency (in Hz) and wavelength (in nm) of the emitted photon when an electron drops from the $n = 4$ to the $n = 2$ energy level in a hydrogen atom.

1.27 The He^+ ion contains only one electron and is therefore a hydrogenlike ion that can be described by the Bohr model. Calculate the wavelengths, in increasing order, of the first four transitions in the Balmer series of the He^+ ion. Compare these wavelengths with the same transitions in a hydrogen atom. Comment on the differences.

1.28 Calculate the radii for the Bohr orbits of a hydrogen atom with $n = 2$ and $n = 3$.

1.29 Scientists have found interstellar hydrogen with quantum number n in the hundreds. Calculate the wavelength of light emitted when a hydrogen atom undergoes a transition from $n = 236$ to $n = 235$. In what region of the electromagnetic spectrum does this wavelength fall?

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1.30 Calculate the frequency of light necessary to eject an electron from the ground state of a hydrogen atom.

Matter Has Wavelike Properties

1.31 What are the wavelengths associated with (a) an electron moving at 1.50×10^8 cm s^{-1} and (b) a 60.0-g tennis ball moving at 1500 cm s^{-1}?

1.32 Thermal neutrons are neutrons that move at speeds comparable to those of air molecules at room temperature. These neutrons are most effective in initiating a nuclear chain reaction among ^{235}U isotopes. Calculate the wavelength (in nm) associated with a beam of neutrons moving at 7.00×10^2 m s^{-1}. (The mass of a neutron is 1.675×10^{-27} kg.)

1.33 Protons can be accelerated to speeds near that of light in particle accelerators. Estimate the wavelength (in nm) of such a proton moving at 2.90×10^8 m s^{-1}. (The mass of a proton is 1.673×10^{-27} kg.)

1.34 What is the de Broglie wavelength, in cm, of a 12.4-g hummingbird flying at 1.20×10^2 mph? (1 mile = 1.61 km.)

1.35 What is the de Broglie wavelength (in nm) associated with a 2.5-g Ping-Pong ball traveling 35 mph?

1.36 Suppose that the uncertainty in determining the position of an electron circling an atom in an orbit is 0.4 Å. What is the uncertainty in the velocity?

1.37 Sketch the probability densities for the first three energy levels of the particle in a one-dimensional box. Without doing any calculations, determine the average value of the position of the particle (x) corresponding to each distribution.

1.38 Calculate the frequency of light required to promote a particle from the $n = 2$ to the $n = 3$ levels of the particle in a one-dimensional box, assuming that $L = 5.00$ Å and that the mass is equal to that of an electron.

1.39 Suppose we used the particle in a one-dimensional box as a crude model for the electron in a hydrogen atom. What value of L would you have to use so that the energy of the $n = 1$ to $n = 2$ transitions in both models would be the same? Is this a reasonable value for the size of a hydrogen atom?

1.40 Consider an electron in a one-dimensional box subject to an electric field E. The potential energy of this system is now

$$V(x) = \begin{cases} \infty & x \le 0; x \ge L \\ -eEx & 0 < x < L \end{cases}$$
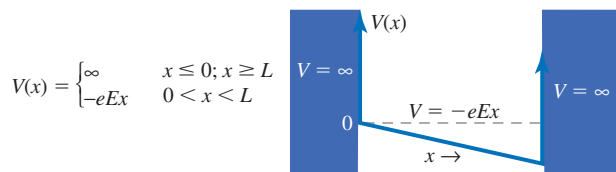
Using what you know about the Schrödinger equation, sketch the wavefunctions for the first three energy levels of this system. What can you predict about the average value of the position of the particle x?

The Hydrogen Atom Is an Exactly Solvable Quantum-Mechanical System

1.41 Give the values of the quantum numbers associated with the following orbitals: (a) 3s, (b) 4p, and (c) 3d.

1.42 Give the values of the quantum numbers associated with the following orbitals: (a) 2p, (b) 6s, and (c) 5d.

1.43 List all the possible subshells and orbitals associated with the principal quantum number $n = 5$.

1.44 List all the possible subshells and orbitals associated with the principal quantum number $n = 6$.

1.45 Calculate the total number of electrons that can occupy (a) one s orbital, (b) three p orbitals, (c) five d orbitals, (d) seven f orbitals.

1.46 Discuss the similarities and differences between a 1s and a 2s hydrogenlike orbital.

1.47 What are the similarities and differences between a 2p_x and a 3p_y hydrogenlike orbital?

1.48 The ionization energy is the energy required to completely remove an electron from the ground state of an atom or ion. Calculate the ionization energies (in kJ mol^{-1}) of the He$^+$ and Li^{2+} ions.

1.49 An electron in the hydrogen atom makes a transition from an energy state of principal quantum number n_1 to the $n = 2$ state. If the photon emitted has a wavelength of 434 nm, what is the value of n_1?

1.50 An electron in a hydrogen atom is excited from the ground state to the $n = 4$ state. Which of the following statements are true and which are false?

(a) The $n = 4$ state is the first excited state.

(b) It takes more energy to ionize (remove) the electron from $n = 4$ than from the ground state.

(c) The electron is farther from the nucleus (on average) in $n = 4$ than in the ground state.

(d) The wavelength of light emitted when the electron drops from $n = 4$ to $n = 1$ is longer than that from $n = 4$ to $n = 2$.

(e) The wavelength of light the atom absorbs in going from $n = 1$ to $n = 4$ is the same as that emitted as it goes from $n = 4$ to $n = 1$.

Additional Problems

1.51 The radioactive Co-60 isotope is used in nuclear medicine to treat certain types of cancer. Calculate the wavelength and frequency of emitted gamma radiation photons having energy equal to 1.29×10^{11} J mol^{-1}.

1.52 When a compound containing cesium ion is heated in a Bunsen burner flame, photons of energy of 4.30×10^{-19} J are emitted. What color is a cesium flame?

1.53 A ruby laser produces radiation of wavelength 633 nm in pulses whose duration is 1.00×10^{-9} s. (a) If the laser produces 0.376 J of energy per pulse, how many photons are produced in each pulse? (b) Calculate the power (in watts) delivered by the laser per pulse. (1 W = 1 J s^{-1}.)

1.54 A 368-g sample of water absorbs infrared radiation at 1.06×10^{4} nm from a carbon dioxide laser. Suppose all the absorbed radiation is converted to energy in the form of heat. Calculate the number of photons at this wavelength required to raise the temperature of the water by 5.00°C. (It takes 4.184 J of heat energy to raise the temperature of 1.00 g of water by 1.00°C.)

1.55 Photodissociation of water

$$H_2O(l) + h\nu \longrightarrow H_2(g) + \frac{1}{2}O_2(g)$$
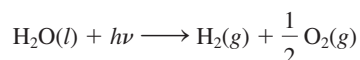
has been suggested as a source of hydrogen. The energy for the reaction is 285.8 kJ per mole of water decomposed. Calculate the maximum wavelength (in nm) that would provide the necessary energy. In principle, is it feasible to use sunlight as a source of energy for this process?

1.56 Spectral lines of the Lyman and Balmer series do not overlap. Verify this statement by calculating the longest wavelength associated with the Lyman series and the shortest wavelength associated with the Balmer series (in nm).

1.57 Only a fraction of the electrical energy supplied to a tungsten lightbulb is converted to visible light. The rest of the energy shows up as infrared radiation (that is, heat). A 75-W light bulb converts 15.0 percent of the energy supplied to it into visible light (assume the wavelength to be 550 nm). How many photons are emitted by the light bulb per second? (1 W = 1 J s^{-1}.)

1.58 Certain sunglasses have small crystals of silver chloride (AgCl) incorporated in the lenses. When the lenses are exposed to light of the appropriate wavelength, the following reaction occurs:

$$AgCl \longrightarrow Ag + Cl$$
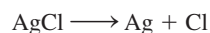
The Ag atoms formed produce a uniform gray color that reduces the glare. If the energy required for the preceding reaction is 248 kJ mol^{-1}, calculate the maximum wavelength of light that can induce this process.

1.59 A student carried out a photoelectric experiment by shining visible light on a clean piece of cesium metal. She determined the kinetic energy of the ejected electrons by applying a retarding voltage such that the current due to the electrons read exactly zero. The condition was reached when $eV = (1/2)m_e u^2$, where e is the electron charge, V is the

retarding voltage, and u is the velocity of the electron. Her results were as follows:

λ (nm)	405.0	435.5	480.0	520.0	577.7	650.0
V (volt)	1.475	1.268	1.027	0.886	0.667	0.381

Rearrange Equation 1.4 to read

$$\nu = \frac{\Phi}{h} + \frac{e}{h}V$$

then determine the values of h and Φ graphically.

1.60 Equations 1.13 and 1.16 were derived assuming that the electron orbits a stationary nucleus; however, this would only be true if the nucleus were of infinite mass. Although the nucleus is much more massive than the electron, it is not infinitely so, and both the nucleus and the electron orbit a common point centered very close to the nuclear position. To correct for this you must replace the mass of the electron in Equations 1.13 and 1.16 with the quantity $\mu = \dfrac{m_e m_N}{m_e + m_N}$, called the *reduced mass,* where m_N is the mass of the nucleus. Calculate the percent change in the Rydberg constants (R_H) for H and He$^+$ using this correction.

1.61 From the exact solution to the Schrödinger equation, the square of the orbital angular momentum of the electron in a hydrogen atom is equal to $l(l + 1)\hbar^2$. (a) What is the orbital angular momentum for an electron in an s orbital? (b) How does this value compare to the Bohr model prediction?

1.62 The sun is surrounded by a white circle of gaseous material called the corona, which becomes visible during a total eclipse of the sun. The temperature of the corona is in the millions of degrees Celsius, which is high enough to break up molecules and remove some or all of the electrons from atoms. One method by which astronomers can estimate the temperature of the corona is by studying the emission lines of ions of certain elements. For example, the emission spectrum of Fe^{14+} ions has been recorded and analyzed. Knowing that it takes 3.5×10^{4} kJ mol^{-1} to convert Fe^{13+} to Fe^{14+}, estimate the temperature of the sun's corona. (*Hint:* The average kinetic energy of 1 mol of a gas is $3/2\,RT$, where the gas constant $R = 8.314$ J mol^{-1} K^{-1} and T is the absolute temperature in kelvin.

1.63 An electron in an excited state in a hydrogen atom can return to the ground state in two different ways: (a) via a direct transition in which a photon of wavelength λ_1 is emitted and (b) via an intermediate excited state reached by the emission of a photon of wavelength λ_2. This intermediate excited state then decays to the ground state by emitting another photon of wavelength λ_3. Derive an equation that relates λ_1, λ_2, and λ_3.

1.64 Alveoli are the tiny sacs of air in the lungs whose average diameter is 5.0×10^{-5} m. Consider an

oxygen molecule (mass $= 5.3 \times 10^{-26}$ kg) trapped within a sac. Calculate the uncertainty in the velocity of the oxygen molecule. (*Hint:* The maximum uncertainty in the position of the molecule is given by the diameter of the sac.)

1.65 How many photons at 660 nm must be absorbed to melt 5.0×10^2 g of ice? On average, how many H_2O molecules does one photon convert from ice to water? (*Hint:* It takes 334 J to melt 1 g of ice at 0°C.)

1.66 The UV light that is responsible for tanning human skin falls in the 320- to 400-nm region. Calculate the total energy (in joules) absorbed by a person exposed to this radiation for 2.0 h, given that there are 2.0×10^{16} photons hitting the surface of Earth per square centimeter per second over an 80-nm (320 nm to 400 nm) range and that the exposed body area is 0.45 m². Assume that only half of the radiation is absorbed and that the remainder is reflected by the body. (*Hint:* Use an average wavelength of 360 nm when calculating the energy of a photon.)

1.67 In 1996 physicists created an antiatom of hydrogen. In such an atom, which is the antimatter equivalent of an ordinary atom, the electrical charges of all the component particles were reversed. Thus, the nucleus of an antiatom is made of an antiproton, which has the same mass as a proton but bears a negative charge, and the electron is replaced by an antielectron (also called positron), which has the same mass as an electron, but bears a positive charge. Would you expect the energy levels, emission spectra, and atomic orbitals of an anti–hydrogen atom to be different from those of a hydrogen atom? What would happen if an antiatom of hydrogen collided with a hydrogen atom?

1.68 In Chapter 5 we will see that the mean velocity of a gas molecule is given by $\sqrt{3RT/\mathcal{M}}$ where T is the absolute temperature, $\mathcal{M}$ is the molar mass, and R is the gas constant ($R = 8.314$ J mol^{-1} K^{-1}). Using this information, calculate the de Broglie wavelength of a nitrogen (N_2) molecule at 300 K.

1.69 When an electron makes a transition between energy levels of a hydrogen atom by absorbing or emitting a photon, there are no restrictions on the initial and final values of the principal quantum number n. However, there is a quantum mechanical rule that restricts the initial and final values of the orbital angular momentum quantum number l. This is the *selection rule,* which states that $\Delta l = \pm 1$, that is, in a transition, the value of l can only increase or decrease by one. According to this rule, which of the following transitions are allowed: (a) $1s \longrightarrow 2s$, (b) $2p \longrightarrow 1s$, (c) $1s \longrightarrow 3d$, (d) $3d \longrightarrow 4f$, (e) $4d \longrightarrow 3s$?

1.70 In an electron microscope, electrons are accelerated by passing them through a voltage difference. The kinetic energy thus acquired by the electrons is equal to the voltage times the charge on the electron. Thus, a voltage difference of 1 volt (V) imparts a kinetic energy of 1.602×10^{-19} volt-coulomb or 1.602×10^{-19} J. Calculate the wavelength associated with electrons accelerated by 5.00×10^3 V.

1.71 (a) An electron in the ground state of the hydrogen atom moves at an average speed of 5×10^6 m s^{-1}. If the speed of the electron is known to an uncertainty of 1 percent, what is the uncertainty in knowing its position? Given that the radius of the hydrogen atom in the ground state is 5.29×10^{-11} m, comment on your result. (b) A 0.15-kg baseball thrown at 100 mph has a momentum of 6.7 kg m s^{-1}. If the uncertainty in measuring the momentum is 1.0×10^{-7} times the momentum, calculate the uncertainty in the baseball's position.

1.72 When two atoms collide, some of their kinetic energy may be converted into electronic energy in one or both atoms. If the average kinetic energy is about equal to the energy for some allowed electronic transition, an appreciable number of atoms can absorb enough energy through an inelastic collision to be raised to an excited electronic state. (a) Calculate the average kinetic energy per atom in a gas sample at 298 K. (b) Calculate the energy difference between the $n = 1$ and $n = 2$ levels in hydrogen. (c) At what temperature is it possible to excite a hydrogen atom from the $n = 1$ level to the $n = 2$ level by collision? (The average kinetic energy of 1 mol of a gas at low pressures is $3/2 \, RT$, where the gas constant $R = 8.314$ J mol^{-1} K^{-1} and T is the absolute temperature in kelvin.)

1.73 Calculate the energies needed to remove an electron from the $n = 1$ state and the $n = 5$ state in the Li^{2+} ion. What is the wavelength (in nm) of the emitted photon in a transition from $n = 5$ to $n = 1$?

1.74 In the beginning of the twentieth century, some scientists thought that the nucleus contained both electrons and protons. Use the Heisenberg uncertainty principle to show that an electron cannot be confined within a nucleus. Repeat your calculation for a proton. Comment on your results. Assume the radius of a nucleus to be 1.0×10^{-15} m. The masses of an electron and proton are 9.109×10^{-31} kg and 1.673×10^{-27} kg, respectively. (*Hint:* Treat the radius of the nucleus as the uncertainty in position.)

1.75 Given a one-dimensional probability density $p(x)$, the average value, $\bar{f}$, of any function of x, $f(x)$, is given by

$$\bar{f} = \int_a^b f(x)\, p(x)\, dx$$

For the particle in a one-dimensional box, a and b are 0 and L, respectively, and $p(x) = |\psi(x)|^2$. For the first three energy levels of the particle in a one-dimensional box, calculate the average values of x and x^2. (*Hint:* You will need to consult a standard table of integrals for this problem.)

1.76 Using the radial probability function, calculate the average values of r for the 1s and 2s orbitals of the hydrogen atom. How do these compare with the most probable values? (*Hint:* You will need to consult a standard table of integrals for this problem.)

1.77 An important property of the wavefunctions of the particle in a one-dimensional box is that they are *orthogonal;* that is,

$$\int_0^L \psi_n(x)\, \psi_m(x)\, dx = 0 \text{ for } n \neq m$$

Show that the wavefunctions defined in Equation 1.35 have this property.

1.78 In the particle in a two-dimensional box, the particle is confined to a rectangular box with side dimensions L_x and L_y. The energy levels for this system are given by

$$E(n_x, n_y, n_z) = \frac{h^2}{8m}\left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2}\right]$$

where the three quantum numbers (n_x and n_y) can be any set of two strictly positive integers. The wavefunction corresponding to the state (n_x, n_y) is

$$\psi(x, y, z) = \left(\frac{4}{L_x L_y}\right)^{\frac{1}{2}}\sin\left(\frac{n_x \pi x}{L_x}\right)\sin\left(\frac{n_y \pi y}{L_y}\right)$$

If the box is a square ($L_x = L_y$), determine the set of two quantum numbers for the five lowest energy levels. (Some energy levels may consist of several degenerate quantum states.) Try to represent the corresponding wavefunctions graphically.

Answers to Practice Exercises

1.1 3.28 m **1.2** 9.94 $\times$ 10^{-16} J **1.3** 264 nm, 304 nm **1.4** 105.9 pm **1.5** 273 nm, UV **1.6** 56.54 nm **1.7** 5.95 $\times$ 10^4 m s^{-1} **1.8** 222 nm **1.9** $n = 5$, $l = 3$, $m_l = -3, -2, -1, 0, +1, +2, +3$