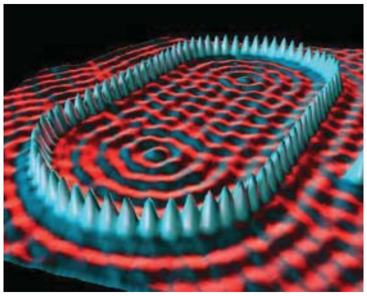


A Brief Review of Quantum Theory

3

> "Anyone who is not shocked by quantum theory has not understood it."
>
> —*Niels Bohr*

3.1 THE WAVELIKE PROPERTIES OF LIGHT

It is a relatively simple matter to observe the macroscopic properties of matter—that is to say, we can measure the mass of a mole of particles or the volume of a gas or the density of a solid. However, if we want to observe a single atom or something on the subatomic level, our powers of observation are limited. At this microscopic level, we are forced to use a form of *spectroscopy*, which deals with the interaction of light with matter. The wavelike properties of light have been well-documented, beginning with the pioneering work of Christiaan Huygens in 1678. In contrast to Newton's corpuscular theory of light, Huygens "wavelets" could better explain certain properties of light, such as reflection, refraction, and diffraction. For mathematical purposes, light can be considered as a sine wave, oscillating in a plane parallel to its direction of travel. The *wavelength* (λ) of light, measured in meters (m) is defined as the distance between successive crests on the wave, while the *frequency* (υ) is the number of times a crest passes a fixed point per unit time (s^{-1}). Thus, the product of the wavelength and the frequency will be equal to its velocity (m/s), as shown by Equation (3.1). One of the most important properties of waves is the principle of *superposition*. Whenever two waves are travelling at the same velocity and in the same direction, the amplitudes of the two waves can be added together to create a new wave front. If the original waves have the same amplitude initially and are exactly in phase with one another, *constructive interference* will occur, leading to a new wave front having a magnitude that is twice that of either of the originals, as shown in Figure 3.1(a). If, on the other hand, the original waves are exactly out of phase with one another and have identical (but opposite) amplitudes, then they will exactly cancel each other out in a process known as *destructive interference*, which is shown in Figure 3.1(b). Of course, it is also possible to mathematically add the sine waves from more than two waves

Quantum corral. [Image originally created by IBM Corporation.]

Principles of Inorganic Chemistry, First Edition. Brian W. Pfennig.

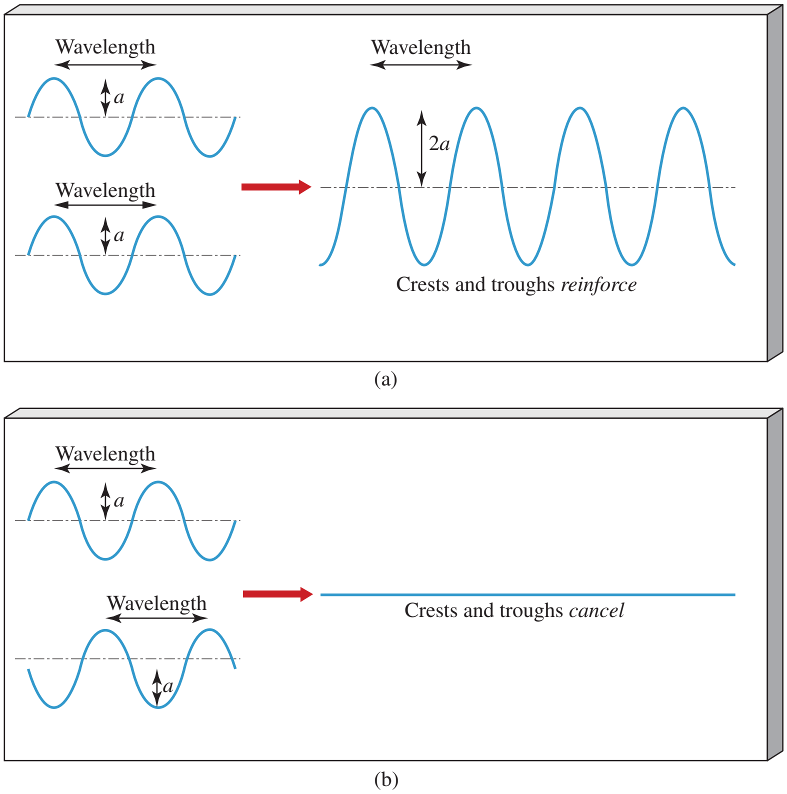


FIGURE 3.1
(a) Constructive and (b) destructive interference of two in-phase light waves. [Reproduced by permission from Astronomy Today, McMillan and Chaisson, 2nd ed., Prentice Hall, 1997.]

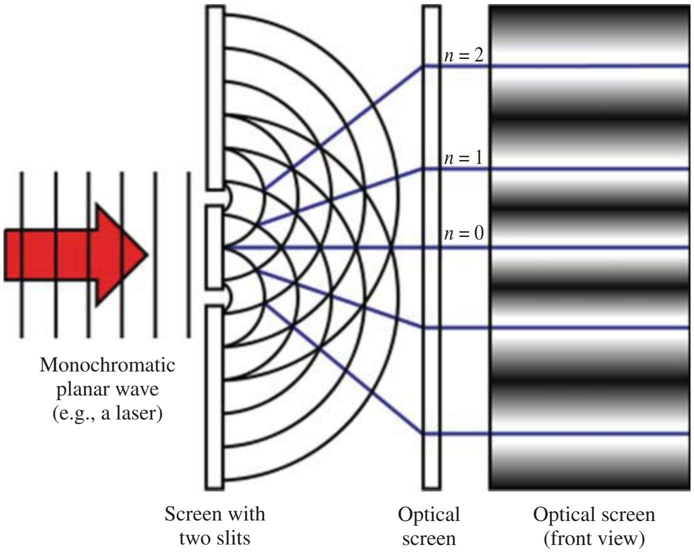


FIGURE 3.2
The interference (or diffraction) pattern that results when two monochromatic beams of light pass through a screen containing two narrow slits and are then observed on a parallel optical screen some distance away from the light source. This experiment, which is known as *Thomas Young's double slit experiment*, demonstrates the wavelike nature of light. [Reproduced from http://en.wikibooks.org/wiki/High_School_Chemistry/The_Dual_Nature_of_Light (accessed November 30, 2013).]

together at any given time, just as it is also possible to add together waves that are not in phase with one another or which have differing initial amplitudes.

$$v = \upsilon\lambda \tag{3.1}$$

In 1801, Thomas Young performed his famous *double slit experiment*, finally proving the wavelike nature of light. A diagram of this experiment is shown in Figure 3.2. A beam of monochromatic light (such as that from a LASER beam) is passed through two narrow openings. As the coherent (in-phase) light waves pass through the holes, they spread out to form a semicircular pattern of propagating wavefronts. This phenomenon is completely analogous to the way that the wake from a passing boat might spread out around a rock in the middle of an otherwise calm reservoir. In the figure, the black concentric circles represent the crests of the wave at any given point in time. Where the two wavefronts are in phase with one another, constructive interference occurs, leading to a larger amplitude (or bright light fringes) on an optical screen that is parallel to the screen containing the two slits. Destructive interference, on the other hand, occurs when the waves are exactly out of phase, causing the amplitudes to cancel with each other and leading to *nodes* (or dark fringes) on the optical screen.

In 1873, building on the work of others, James Clerk Maxwell published his comprehensive theory of electromagnetic radiation in *A Treatise on Electricity and Magnetism*. In his book, Maxwell argued that light can be thought of as a transverse wave that consists of perpendicularly oscillating electric (E) and magnetic (B) fields that each lie perpendicular to the direction of travel, as shown in Figure 3.3. Light travelling in a vacuum travels at the speed of light, which is defined as follows: $c \equiv 2.99792458 \times 10^8$ m/s. Substituting c for v in Equation (3.1) yields the more familiar Equation (3.2). The different types or colors of *electromagnetic radiation* can be classified according to either their wavelengths or their frequencies, as shown in Figure 3.4.

$$c = \upsilon\lambda = 2.99792458 \times 10^8 \text{ m/s} \tag{3.2}$$

Example 3-1. The standard garage door opener typically operates at a frequency of about 400 Hz ($1 \text{ Hz} = 1 \text{ s}^{-1}$). Calculate the wavelength for this frequency of light and identify to which region of the electromagnetic spectrum it belongs.

Solution. Solving Equation (3.2) for the wavelength, one obtains:

$$\lambda = \frac{c}{\nu} = \frac{2.99792458 \times 10^8 \text{ m/s}}{400\,(1/\text{s})} = 0.750 \text{ m}$$

This wavelength falls in the microwave region of the electromagnetic spectrum.

At Ursinus College, where I teach, there is a training drill that the football team uses called the *ropes exercise*. With one end of a heavy rope affixed to the wall, the football player swings the other end of the rope up and down, creating a transverse wave in the rope, as shown in Figure 3.5. Initially, the wave travels from the football

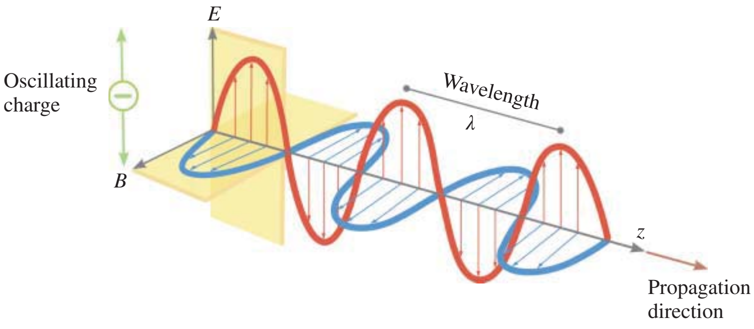


FIGURE 3.3
Maxwell's depiction of a light wave as perpendicularly oscillating electric (E) and magnetic (B) fields. [Blatt Communications.]

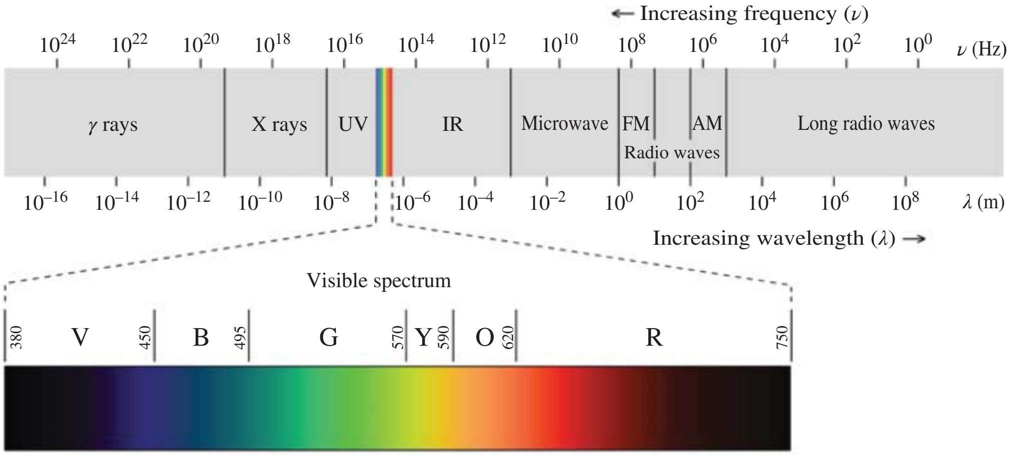


FIGURE 3.4

The electromagnetic spectrum, showing an expansion of the visible region in color. [Attributed to Philip Ronan under the Creative Commons Attribution-Share Alike 3.0 Unported license (accessed October 17, 2013).]

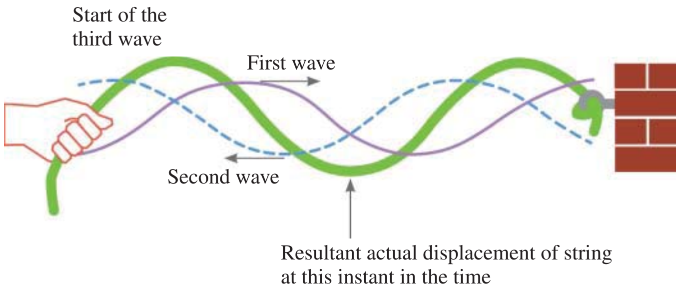


FIGURE 3.5

Schematic diagram of the ropes exercise, where one end of the rope is fixed while the football player initiates a transverse wave in the rope by an up-and-down motion. [Blatt Communications.]

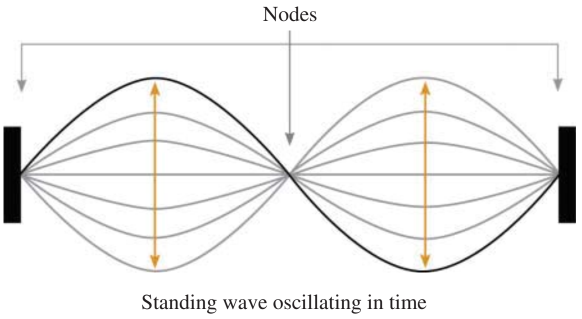


FIGURE 3.6

An example of a standing wave such as the one produced when a guitar string is plucked. [Blatt Communications.]

player in the direction of the wall, where it is then reflected. As the wave returns toward the football player, it encounters another wave (which may or may not be in phase with the original wave) and the two waves interfere with one another.

Now suppose instead of fixing just one end of the rope, a lighter string is used where both ends of the rope are fixed. This phenomenon occurs across campus in the music department whenever a musician plucks a guitar string or creates a vibration in the string of a violin. This creates an entirely different kind of wave than the ropes drill. Once the initial perturbation is introduced into the string, creating amplitude along the *y*-direction, for instance, the string will begin to oscillate at a characteristic frequency, as shown in Figure 3.6.

In order to sustain the note and to create music, only those wavelengths that have an amplitude of zero at both ends of the fixed string can constructively interfere with one another to create what is known as a *standing wave*. A *standing wave* (also called a *stationary wave*) is a wave that exists in a fixed position. Although the standing wave appears to be stationary, it is actually oscillating up and down in place as a function of time. Therefore, the amplitude of the wave (y) is a function of its position (x) and time (t), as shown in Equation (3.3). This is the classical wave equation in one-dimension (see Appendix A for a derivation).

$$\frac{\partial^2 y}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 y}{\partial t^2} \tag{3.3}$$

The wave equation is a linear, second-order partial differential equation. While the solution to this type of differential equation is not particularly difficult, it might present a challenge for the average student taking inorganic chemistry. Therefore, a general solution is presented and it is left as an exercise to demonstrate the validity of this result. One possible solution to the one-dimensional wave equation is the sine wave given by Equation (3.4), where A is the maximum amplitude of the wave.

$$y(x,t) = A\sin\left[2\pi\left(\frac{x}{\lambda} - \nu t\right)\right] \tag{3.4}$$

Example 3-2. Prove that Equation (3.4) is a solution to the one-dimensional classical wave equation given in Equation (3.3).

Solution. Taking the first partial derivative of y with respect to x and t yields the following:

$$\frac{\partial y}{\partial x} = \frac{2\pi}{\lambda}A\cos\left[2\pi\left(\frac{x}{\lambda} - \nu t\right)\right]$$

$$\frac{\partial y}{\partial t} = -2\pi\nu A\cos\left[2\pi\left(\frac{x}{\lambda} - \nu t\right)\right]$$

Now, taking the second partial derivative of y with respect to x and t yields:

$$\frac{\partial^2 y}{\partial x^2} = -\left(\frac{2\pi}{\lambda}\right)^2 A\sin\left[2\pi\left(\frac{x}{\lambda} - \nu t\right)\right] = -\left(\frac{2\pi}{\lambda}\right)^2 y(x,t)$$

$$\frac{\partial^2 y}{\partial t^2} = -(2\pi\nu)^2 A\sin\left[2\pi\left(\frac{x}{\lambda} - \nu t\right)\right] = -(2\pi\nu)^2 y(x,t)$$

Operators such as this that yield back the original function times a constant are called *eigenfunctions* and the corresponding constants are known as the *eigenvalues*. You will find that most of the operators in quantum mechanics will be of this type. Substituting the second partial derivatives into Equation (3.3) and cancelling the signs yields

$$\left(\frac{2\pi}{\lambda}\right)^2 y(x,t) = \frac{1}{v^2}(2\pi\nu)^2 y(x,t)$$

which reduces to

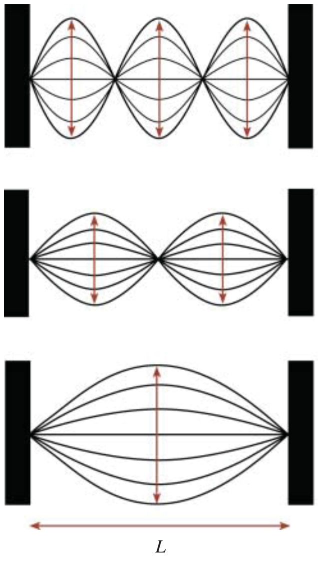
$$\frac{1}{\lambda^2} = \frac{\nu^2}{v^2}$$

Taking the square root of both sides yields the equality given by Equation (3.1).

By introducing the constraint that the amplitude of the wave must be zero at both ends of the string in order to have constructive interference, we have imposed a set of *boundary conditions* on the mathematical problem, namely, that $y(0, t) = y(L, t) = 0$ at any value of t, where L is the length of the string. Because this must be true for any value of t, we can arbitrarily set $t = 0$ to simplify the math, so that $A \sin(0) = A \sin(2\pi L/\lambda) = 0$. Ignoring the trivial solution that $A = 0$ and recognizing that $\sin(n\pi) = 0$ whenever n is an integer, we obtain the result that $\lambda = 2L/n$. As this example demonstrates, the concept of *quantization* (integral values of n) arises naturally whenever we force the ends of the string to be fixed in place. Several of the standing wave solutions for different values of n are depicted in Figure 3.7. One feature that is common to all of the solutions is the presence of nodes (where the amplitude is always zero) and the presence of antinodes (where the amplitude reaches its maximum value).

The lowest frequency occurs when $n = 1$ and is called the *fundamental*. Doubling the frequency corresponds to raising the pitch by an octave. Those solutions having values of $n > 1$ are known as the *overtones*. As mentioned previously, one important property of waves is the concept of superposition. Mathematically, it can be shown that any periodic function that is subject to the same boundary conditions can be represented by some linear combination of the fundamental and its overtone frequencies, as shown in Figure 3.8. In fact, this type of mathematical analysis is known as a *Fourier series*. Thus, while the note middle-A on a clarinet, violin, and piano all have the same fundamental frequency of 440 Hz, the sound (or timbre) that the different instruments produce will be distinct, as shown in Figure 3.9.

If electromagnetic radiation can be considered a wave, then what exactly is it that is doing the waving? Imagine a cork bobbing up and down on the surface of a reservoir as a result of the wave from a passing boat. To a first approximation, the cork will not change its longitudinal or latitudinal position. It will simply oscillate up and down in position as the wavefront passes by. Now, imagine the opposite scenario, where a cork is forced to oscillate in a periodic manner on the surface of a smooth body of water. The periodic motion of the cork will lead to the generation of waves in the liquid. By analogy, light can be produced by an oscillating charge, such as an electron (or for that matter any charged particle) being accelerated back and forth between two poles (e.g., in a radio transmission tower).



Harmonic	n	No. of nodes	λ	ν
Second overtone	3	4	$2L/3$	$3\nu 1$
First overtone	2	3	$2L/2$	$2\nu 1$
Fundamental	1	2	$2L$	$\nu 1$

FIGURE 3.7
Several solutions to the wave equation subject to the boundary conditions for a standing wave that $y(0,t) = y(L,t) = 0$. [Blatt Communications.]

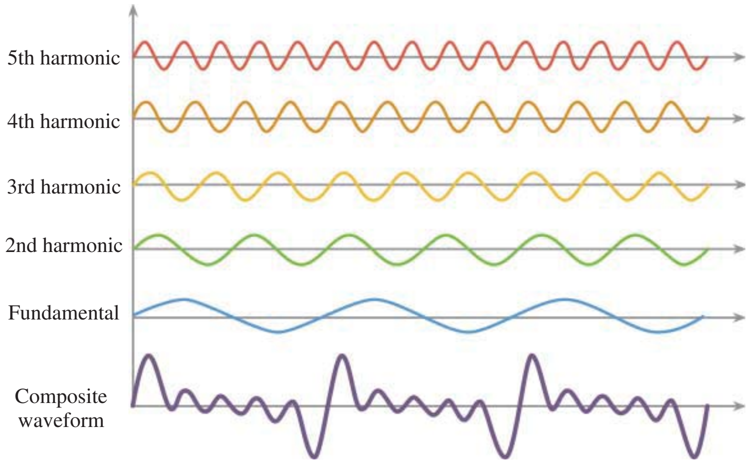


FIGURE 3.8
A composite periodic waveform can be constructed from a linear combination of the fundamental and its overtones (or partials). [Blatt Communications.]

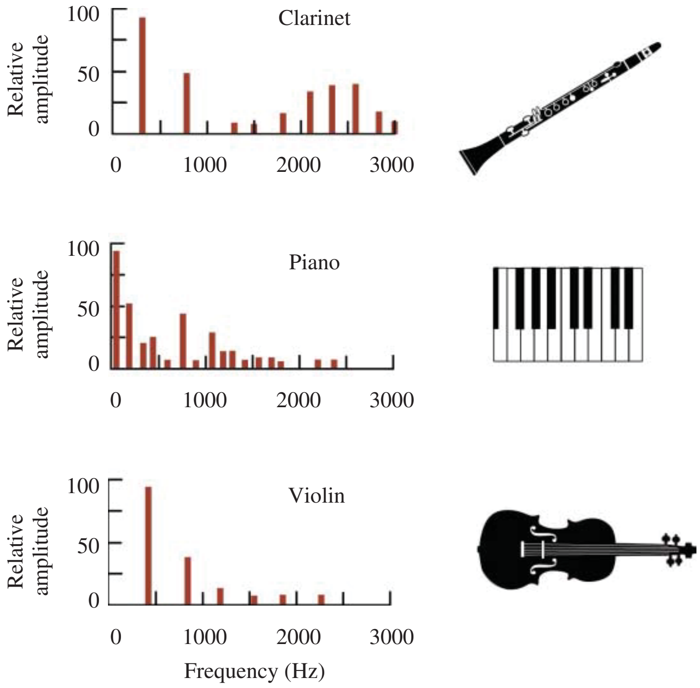


FIGURE 3.9
Illustration of how the timbre of different musical instruments playing the same note can produce distinctly different sounds depending on the exact combination of the fundamental and its overtones. [Blatt Communications.]

Now suppose that a cork was floating peacefully on the surface of a perfectly smooth body of water. Then along comes the wake from a passing motorboat. What will happen? The cork will begin to oscillate up and down in a periodic manner as the wavefronts from the motorboat pass by in the water underneath it. In a similar manner, the interaction of light with matter can cause oscillations of the charged particles within the substance. Low-frequency radiation, such as infrared light, can cause the positions of the atoms in molecules to vibrate, whereas high-frequency radiation, such as ultraviolet light, can effect electronic transitions or even ionization. Therefore, the different regions of the electromagnetic spectrum can be used to probe various aspects of a molecule's fundamental structure. This serves as the basis for the field of atomic and molecular spectroscopy.

3.2 PROBLEMS WITH THE CLASSICAL MODEL OF THE ATOM

The quantization of matter has been generally accepted as fact since John Dalton's atomic theory was published in 1808. Dalton's theory of the atom consisted of four fundamental axioms:

- *Matter is composed of tiny, indivisible particles called atoms*. Although it is now recognized that the atom is itself composed of smaller subatomic particles, this fact does little to change the essence of Dalton's original statement.
- *Elements can be distinguished from one another based on the masses of their atoms*. This statement is also incorrect, because isotopes with different mass numbers often exist for the same element. An element is now characterized by the number of protons it contains in its nucleus.
- *Atoms can neither be created, nor destroyed*. This assertion is also false, because the transformation of one element into another is a regular occurrence in nuclear chemistry.
- *When the elements combine in a chemical reaction, they do so in small, whole-number ratios*. This final point is simply a restatement of Proust's law of definite proportions.

The importance of Dalton's work is that it was based on the scientific method. Dalton realized that air and evaporated water consisted of fundamentally different gases; and it was his experiments using mixtures of gases that led him to the conclusion that the gases themselves must be composed of particles having different sizes. In other words, matter must be quantized—composed of small, individual particles having definite sizes and masses.

It was not until a century later, however, that energy was first considered to be quantized. On December 14, 1900, Max Planck delivered his landmark address at a meeting of the German Physical Society where he suggested that the spectral distribution of blackbody radiation could only be explained if matter absorbs and emits energy in discrete amounts. It had long been recognized that certain metallic objects, when heated, radiated light having a characteristic spectrum, such as the one shown in Figure 3.10. Furthermore, the exact distribution of wavelengths radiated by the heated object depended on its temperature. As the temperature increases, the wavelength having the largest intensity gradually shifts from longer (red) to shorter (blue) wavelengths. Strictly speaking, a *blackbody* is an idealized object that can perfectly absorb and emit radiation of all frequencies. One of the closest real-world approximations to a blackbody radiator is a star. The spectral distribution (intensity vs wavelength profile) of a star is analogous to that of an ideal blackbody, with the wavelength of its maximum intensity decreasing with increasing temperature. This explains why a cooler star (~3000 K) has a red appearance, while the hottest of stars (>5000 K) are blue, as shown in Figure 3.10.

The distribution curve for a blackbody that is predicted by classical physics is also shown in Figure 3.10. This curve is based on the *Rayleigh–Jeans law*, which is given by Equation (3.5), where ρ is the energy density per frequency (proportional to the intensity axis shown in Figure 3.10), k_B is the Boltzmann constant ($k_B = R/N_A = 1.381 \times 10^{-23}$ J/K), and T is the absolute temperature (K). At long wavelengths, there is a fairly good agreement between the experimental and predicted distribution curves for a blackbody having $T = 5000$ K. However, at shorter wavelengths, the classical prediction clearly deviates from observation. Because this deviation begins to occur at wavelengths that fall in the ultraviolet range of the electromagnetic spectrum, this

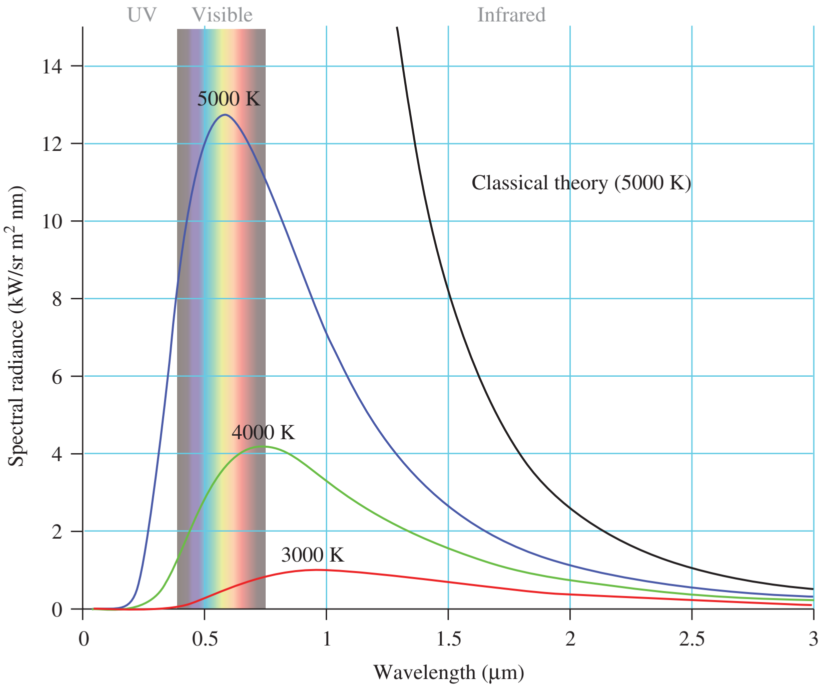


FIGURE 3.10

The spectral distribution of radiation as a function of wavelength for three different temperature stars. A star is one of the closest approximations to a perfect blackbody radiator. [Reproduced from http://en.wikipedia.org/wiki/Black-body_radiation (accessed October 17, 2013).]

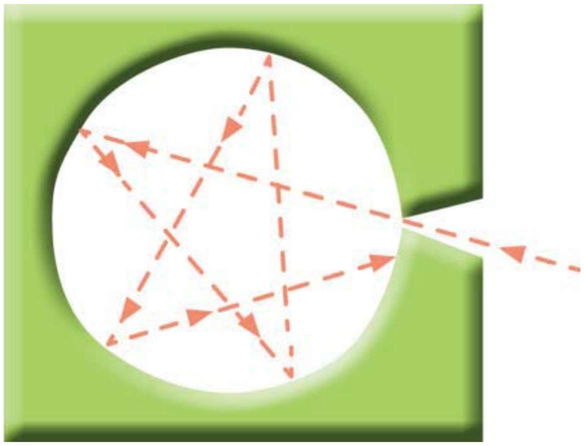


FIGURE 3.11

Analogy of a perfect blackbody with a hollow metal cavity having a tiny pinhole. [Blatt Communications.]

shortcoming of classical theory is often referred to as the *UV catastrophe*.

$$\rho_\nu(T)\,\mathrm{d}\nu = \frac{8\pi\nu^2 k_\mathrm{B} T}{c^3}\mathrm{d}\nu \tag{3.5}$$

According to classical mechanics, the absorption of heat by a metal object leads to an increase in the kinetic energy of its constituent atoms. As the energy is absorbed, it causes the electrons and charged nuclei in the solid to oscillate back and forth with characteristic frequencies. To a first approximation, an idealized blackbody will behave like a hollow cavity with a small pinhole in it, as the one depicted in Figure 3.11. When the object is heated or absorbs electromagnetic radiation, the total energy is forced to equilibrate inside the cavity before any radiation can be emitted through the pinhole in the form of light. As was shown in Section 3.1, the boundary conditions for constructive interference of standing waves in a cavity

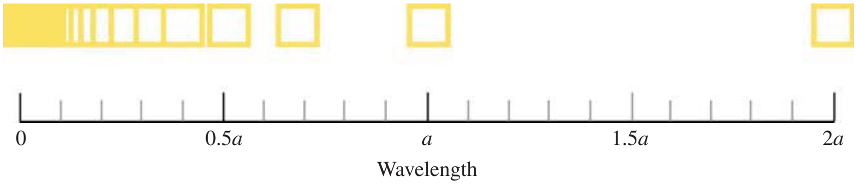


FIGURE 3.12
Illustration of how the number of allowed oscillators increases as the wavelength decreases. [Blatt Communications.]

of diameter L requires that $\lambda = 2L/n$, where n is a positive integer. Thus, only certain wavelengths of oscillations may exist as standing waves. The wavelengths and shapes of the allowed standing waves are therefore the same as those shown in Figure 3.7. Because of the inverse relationship between λ and n, the probability density of allowed oscillations increases at shorter wavelengths, as shown in Figure 3.12, where $a = L$. Classical physics predicted that the total energy absorbed by all the vibrations of the charged particles inside a blackbody would be equally distributed over all of the allowed oscillators. This is known as the *equipartition of energy*. In other words, there were no special rules imparted to make some of the oscillations more favorable than others. Thus, the intensity of the electromagnetic radiation emitted through the pinhole would necessarily increase at shorter and shorter wavelengths, simply because there is a higher density of allowed wavelengths at shorter wavelengths.

Planck overcame this limitation by postulating that the energies of the oscillations could only exist in discrete amounts, with the energy (E) of a given oscillation being directly proportional to its frequency, according to Equation (3.6), where h is Planck's constant ($h = 6.6261 \times 10^{-34}$ J s). Borrowing from the statistical work of Boltzmann, those oscillators requiring more energy to vibrate would necessarily have a lower probability of occurrence. Because frequency (υ) and wavelength (λ) are inversely proportional to each other through Equation (3.2), the shorter the wavelength, the less probable would be its occurrence. Therefore, even though there is still a higher density of oscillators having short wavelengths, the probability that these short-wavelength oscillators will absorb enough energy to be populated will eventually begin to decrease. The bottom line is that the results of the Planck distribution law, which is given by Equation (3.7), perfectly match those of the experimental curve!

$$E = h\upsilon \tag{3.6}$$

$$\rho_\nu(T)\,\mathrm{d}\nu = \frac{8\pi h k_\mathrm{B} T}{c^3}\,\frac{\nu^3 \mathrm{d}\nu}{e^{h\nu/k_\mathrm{B}T} - 1} \tag{3.7}$$

The essential mathematical substitution made by Planck was the recognition that the energy differences between the allowed oscillations in the solid were quantized, as shown in Figure 3.13. As a result, there were certain rules that had to be introduced in order to govern how much of the total energy a specific oscillator was able to absorb. Another way of thinking about the distribution problem is to consider an old-fashioned coin scramble. Suppose that there is a total of \$9.00 worth of coins (a certain total amount of absorbed energy) to distribute among three very eager children (three of the allowed standing waves or oscillators in Figure 3.13). There are \$3.00 worth of quarters (12 quarters), \$3.00 worth of nickels (60 nickels), and \$3.00 worth of pennies (300 pennies). In the absence of any special rules (no quantization of energy), each of the children will pick up exactly 4 quarters, 20 nickels, and 100 pennies for a total of \$3.00 each. This is the classical analogy to the equipartition of energy—each of the children (oscillators) acquired the same total amount of money (energy). Next, the coin scramble is repeated; but as the organizer, Planck imposes

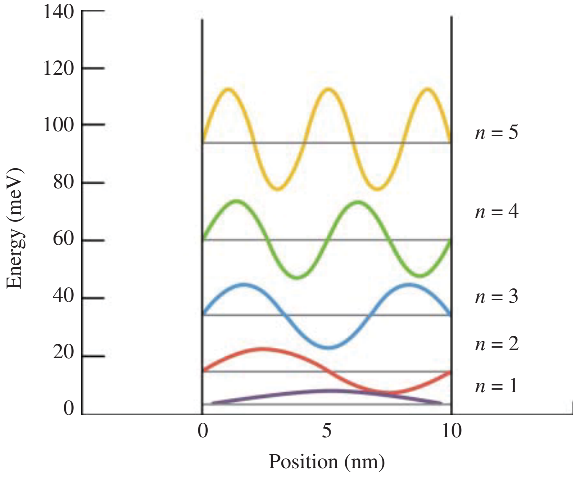


FIGURE 3.13 Energy level diagram for the different allowed vibrations of an oscillating string, showing how the energy increases with *n*. According to Boltzmann's statistical population theorem, low-frequency oscillations will be populated (or occur) more often than higher frequency ones. [Blatt Communications.]

some rules on the game: the first child is not picky and can pick up any denomination of currency, but the second child is a little more discerning and refuses to bend over to pick up any pennies, and finally the third child comes from an exceedingly snobbish background and will only stoop to pick up quarters.

The final results of this second coin scramble are given in Table 3.1. Notice that the rules (or quantum restrictions) that Planck placed on the coin scramble led to an unequal distribution of wealth among the three participants. The restriction that the third child could only acquire the largest denomination of currency led him/her to a smaller take of the total amount of money, just as those oscillators that required a larger quantum jump were less populated in the equilibrium distribution of energy. As it turns out, these are the oscillations with smaller wavelengths; and therefore the intensity profile of Planck's distribution curve follows the Rayleigh–Jeans law at longer wavelengths, but then curves back downward as the wavelength gets shorter.

At first, the implications of the quantization of energy were not fully appreciated. Planck himself was reluctant to accept the concept, convinced that it was merely a mathematical coincidence and that a more satisfactory classical description would eventually replace it. Quoting Banesh Hoffmann in *The Strange Story of the Quantum*, the scientists "could but make the best of it, and went around with woebegone faces sadly complaining that on Mondays, Wednesdays, and Fridays they must look on light as a wave: on Tuesday, Thursdays, and Saturdays as a particle. On Sundays, they simply prayed."

It was not until 5 years later (in 1905) when Albert Einstein explained the photoelectric effect that the concept of quantization looked as if it had any real staying

TABLE 3.1 Results of the coin scramble with and without Planck's special rules.

	Equal Chance (No Rules)			Planck's Rules		
Distribution of coins:	#1	#2	#3	#1	#2	#3
Pennies	100	100	100	300	0	0
Nickels	20	20	20	30	30	0
Quarters	4	4	4	4	4	4
Total amount ($)	3.00	3.00	3.00	5.50	2.50	1.00

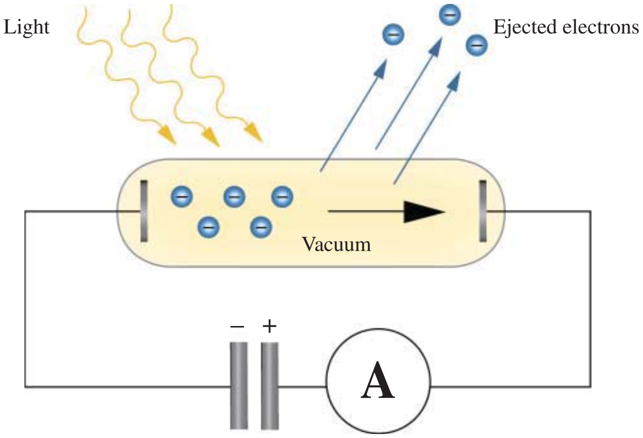


FIGURE 3.14
The photoelectric effect: light striking a metal surface in an evacuated chamber can eject electrons from the metal if the frequency of the light is greater than the work function for the metal. [Blatt Communications.]

power. In 1887, Heinrich Hertz had observed that UV light can eject electrons from a metal plate in a partially evacuated tube (Figure 3.14). There were three major observations associated with this phenomenon. (i) While the kinetic energy of the ejected electrons depended on the frequency, the number of ejected electrons was dependent on the intensity of the light. (ii) There was a certain threshold frequency, characteristic of the metal, below which no electrons at all would be ejected, regardless of the intensity of the light, as shown in Figure 3.15. (iii) There was no lag time between the time the light struck the metal plate and the time that the electrons were ejected. Each of these observations was in direct conflict with the predictions of classical theory. Because the intensity of light (according to Maxwell's equations) is proportional to the square of the amplitude of its electric field, the classical prediction was that the kinetic energy of the electrons should depend on the intensity of the light, not on its frequency. Furthermore, before an electron could be ejected, it was expected that a sufficient amount of energy must be accumulated in order to overcome the surface potential and yet no lag time was observed. Lastly, there was no classical explanation for the threshold energy.

Only by assuming that light behaved as packets of energy did could Einstein explain the experimental data. Einstein originally called these *quanta*, while the modern term for them is *photons*. Furthermore, the energy of each photon was directly related to its frequency through the same proportionality constant, *h*, that Planck had used in his explanation of blackbody radiation. Only those photons having sufficient energy to overcome the work function (ϕ) of the metal (or its ionization energy) would be capable of ejecting an electron. The kinetic energy (KE) of the ejected electron was therefore dependent on the frequency of the photon, as shown by Equation (3.8). The number of ejected electrons, in turn, depended on the intensity

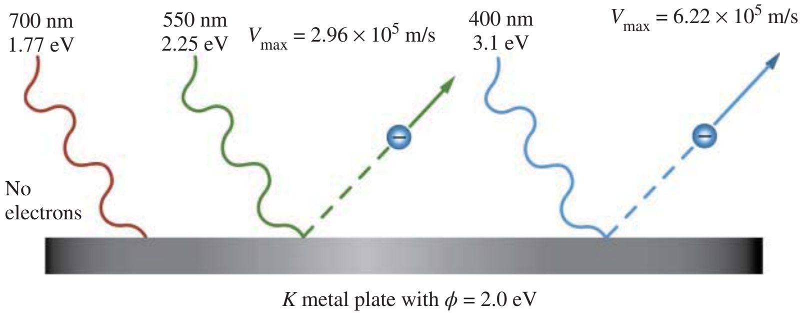


FIGURE 3.15
The photoelectric effect illustrated for potassium metal in a partially evacuated tube. The work function required for the ejection of electrons from a potassium surface is 2.0 eV. Therefore, a photon of red light ($h\nu$ = 1.77 eV) does not have sufficient energy to eject an electron. Photons of green or blue light, which have energies greater than 2 eV, can both eject electrons; but the kinetic energies of the ejected electrons will differ. [Blatt Communications.]

of light, or the number of photons striking the metal surface. Thus, for every photon striking the surface (as long as $h\nu > \phi$), one electron would be ejected. In other words, energy (in the form of electromagnetic radiation) can be considered to have particle-like properties.

$$\mathrm{KE} = h\nu - \phi \tag{3.8}$$

Example 3-3. Potassium has a work function, $\phi = 2.0$ eV. Calculate the velocity of an electron ejected from potassium using blue light with a wavelength of 400 nm.

Solution. The energy of a photon of blue light is directly proportional to its frequency. Combination of Equations (3.6) and (3.2) yields

$$E = \frac{hc}{\lambda} = \frac{(6.6261 \times 10^{-34}\ \mathrm{J\,s})(2.998 \times 10^{8}\ \mathrm{m/s})}{(400\ \mathrm{nm})(1\ \mathrm{m}/10^{9}\ \mathrm{nm})} = 4.97 \times 10^{-19}\ \mathrm{J}$$

Given that 1 eV = 96,485 J/mol and $N_A = 6.022 \times 10^{23}\ \mathrm{mol}^{-1}$:

$$E = 4.97 \times 10^{-19}\ \mathrm{J}\left(\frac{1\ \mathrm{eV}}{96,485\ \mathrm{J/mol}}\right)(6.02 \times 10^{23}\ \mathrm{mol}^{-1}) = 3.10\ \mathrm{eV}$$

Using Equation (3.8), the kinetic energy of the ejected electron is

$$\mathrm{KE} = h\nu - \phi = 3.10\ \mathrm{eV} - 2.0\ \mathrm{eV} = 1.1\ \mathrm{eV}$$

$$\mathrm{KE} = 1.1\ \mathrm{eV}\left(\frac{96,485\ \mathrm{J/mol}}{1\ \mathrm{eV}}\right)\left(\frac{1\ \mathrm{mol}}{6.022 \mathrm{x} 10^{23}}\right) = 1.8 \times 10^{-19}\ \mathrm{J}$$

Because $\mathrm{KE} = (1/2)mv^2$, rearrangement to solve for v yields

$$v = \sqrt{\frac{2\mathrm{KE}}{m_\mathrm{e}}} = \sqrt{\frac{2(1.8 \times 10^{-19}\ \mathrm{J})}{9.11 \times 0^{-31}\ \mathrm{kg}}} = 6.2 \times 10^{5}\ \mathrm{m/s}$$

The first model of the atom to include the concept of quantization was proposed by Niels Bohr in 1913. Before this time, the prevailing notion was that the atom consisted of a dense, positively charged nucleus, about which the electrons orbited much like the planets orbit around the sun. One of the inherent contradictions with the *planetary model* was that the negatively charged electrons should undergo a constant acceleration by virtue of their electrostatic attraction to the nucleus. At the same time, Maxwell's theory of electromagnetism requires that any charged particle undergoing acceleration must continuously emit light. In fact, classical calculations predicted that the electron in a hydrogen atom should rapidly collapse into the nucleus in a matter of several nanoseconds. This, of course, does not occur. Furthermore, the gradual loss of energy as the electron's orbit spirals in closer and closer to the nucleus should lead to an emission spectrum that resembles a continuum of many different wavelengths.

In fact, it had been known for several decades that when certain metal cations are heated in a Bunsen burner, they will emit light of a characteristic color. These are the common flame tests of a qualitative general chemistry laboratory and that form the basis for the different colors in fireworks. For instance, Li^+ and

Sr^{2+} are red, Na^{+} is yellow-orange, and Ba^{2+} is green. Instead of a continuum, as would have been predicted by classical theory, each ion emitted light with a characteristic fingerprint of narrow wavelengths (or lines) when passed through a prism. The line spectrum of hydrogen was well established at the time and is shown in Figure 3.16. In 1885, a Swiss math teacher named Johann Balmer noticed the mathematical pattern in the spectral lines of hydrogen in the visible spectrum and derived an empirical equation to explain them. Then, in 1888, the Swedish physicist Johannes Rydberg generalized the Balmer equation to include several other series of lines that were discovered in the UV and near-IR regions of the hydrogen line spectrum (shown in Figure 3.17). The Rydberg formula, shown in Equation (3.9), can be used to calculate the wavenumber ($1/\lambda$) of any line in the emission spectrum of hydrogen, where R_H is the Rydberg constant and n_f and n_i are both positive integers (with $n_f < n_i$). Each series of lines converges at short wavelengths on what is known as the *series limit*. Because the series limit occurs at the shortest wavelength in each series (or the largest wavenumber), the value of n_i for the

FIGURE 3.16
The line spectrum of hydrogen in the visible region. [Reproduced from http://en.wikipedia.org/wiki/Hydrogen_spectral_series (accessed November 30, 2013).]

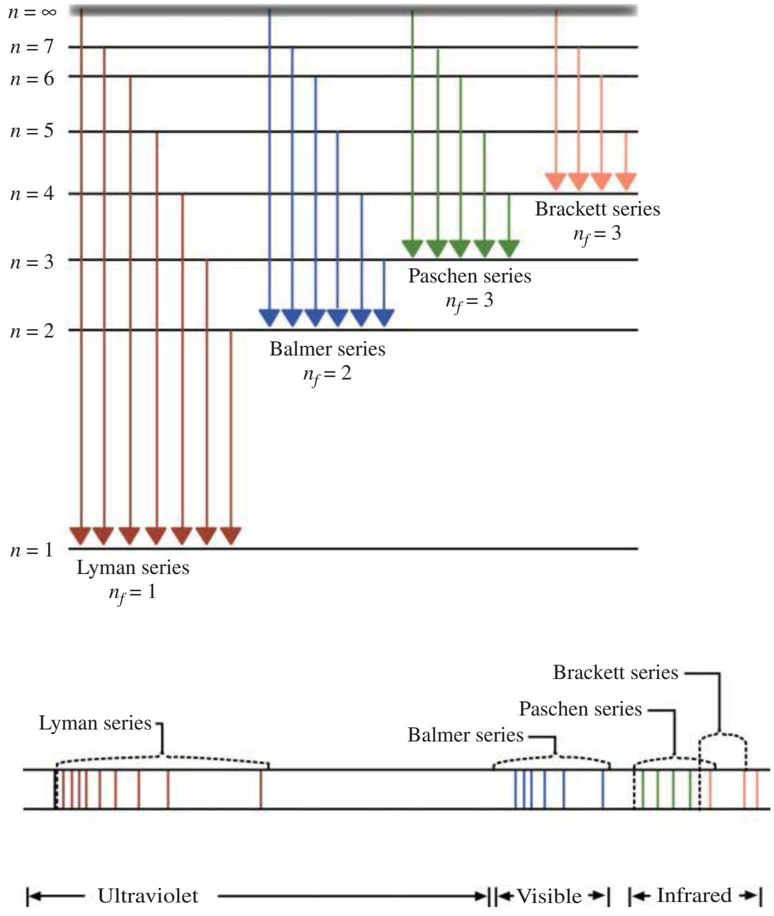


FIGURE 3.17
The complete line spectrum of hydrogen from the ultraviolet to the infrared. Transitions from the $n_i = \infty$ energy level to the lowest energy level in each series correspond with the series limit, where the individual energy levels all start to blur together. [Blatt Communications.]

series limit is always taken as infinity. While mathematically convenient, the Rydberg equation was entirely an empirical equation in desperate need of a more theoretical explanation.

$$\bar{\nu} = \frac{1}{\lambda} = R_H\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right), \text{ where } R_H = 109{,}678\,\text{cm}^{-1} \text{ and } n_f < n_i \tag{3.9}$$

Example 3-4. Calculate the wavelengths (nm) of the five lines shown in Figure 3.16 for the line spectrum of hydrogen if $n_f = 2$ for the Balmer series.

Solution. Using Equation (3.9) with $n_f = 2$ and $n_i = 3$, the wavenumber of the red line in the Balmer series is determined to be 1.52×10^4 cm^{-1}:

$$\bar{\nu} = \frac{1}{\lambda} = 109{,}678\,\text{cm}^{-1}\left(\frac{1}{2^2} - \frac{1}{3^2}\right) = 1.52 \times 10^4\,\text{cm}^{-1}$$

The wavelength of this line is obtained by taking the reciprocal of the wavenumber and then converting from cm into nm, as follows:

$$\lambda = \frac{1}{\bar{\nu}} = \frac{1}{1.52 \times 10^4\,\text{cm}^{-1}} = 6.56 \times 10^{-5}\,\text{cm}\left(\frac{1\,\text{m}}{100\,\text{cm}}\right)\left(\frac{10^9\,\text{nm}}{1\,\text{m}}\right) = 656\,\text{nm}$$

Using $n_i = 4$, 5, 6, and 7, the resulting wavelengths for the remaining lines are 486, 434, 410, and 397 nm, respectively.

Example 3-5. The wavelength of the series limit for the Pfund series of lines in the hydrogen spectrum is 2.28 μm. Determine n_f for the Pfund series and then calculate the longest wavelength line for this series.

Solution. Because $n_i = \infty$ for the series limit, the second term in parentheses in Equation (3.9) approaches zero.

$$\frac{1}{\lambda} = \frac{109{,}678\,\text{cm}^{-1}}{n_f^2} = \frac{1}{2.28\,\mu\text{m}}\left(\frac{10^6\,\mu\text{m}}{1\,\text{m}}\right)\left(\frac{1\,\text{m}}{100\,\text{cm}}\right) = 4390\,\text{cm}^{-1}$$

$$n_f^2 = \frac{109{,}678\,\text{cm}^{-1}}{4390\,\text{cm}^{-1}} = 25 \quad \text{so} \quad n_f = 5$$

3.3 THE BOHR MODEL OF THE ATOM

In the summer of 1912, Niels Bohr wrote to his younger brother Harald: "Perhaps I have found out a little about the structure of atoms." His revolutionary model of the atom was published the following year. In an attempt to develop a theoretical model of the hydrogen atom that was consistent with the lines predicted by the Rydberg formula, Bohr proposed the following:

- The electron moves around the nucleus in circular orbits, where the centripetal and centrifugal forces are exactly balanced. The centrifugal force results from the electrostatic attraction of the negatively charged electron for the positively charged proton in the nucleus and can be calculated according to Coulomb's law. The electron's centripetal motion is governed by Newton's second law. The two forces are set equal in Equation (3.10), where F is the force, e is the electronic charge = 1.602×10^{-19} C, r is the radius, $4\pi\varepsilon_0$ is the permittivity of free space = 1.113×10^{-12} C^2/Nm^2, and r is the radius of the orbit.

$$F = \frac{e^2}{4\pi\varepsilon_0 r^2} = ma = \frac{mv^2}{r}$$

$$\text{(Coulomb's law)} \qquad \text{(Newton's 2nd law)} \tag{3.10}$$

- *The stationary state assumption*: In a given orbit, the total energy (kinetic + potential) will be a constant. The kinetic energy KE is equal to $(1/2)mv^2$, while the potential energy V can be obtained by integrating Coulomb's law with respect to distance. While this assumption was in opposition to the classical prediction that the electron will spiral into the nucleus, it was necessary in order to explain the experimental observations.

$$E = \mathrm{KE} + V = \frac{1}{2}mv^2 + \int \frac{e^2}{4\pi\varepsilon_0^2 r^2}\mathrm{d}r = \frac{1}{2}mv^2 - \frac{e^2}{4\pi\varepsilon_0^2 r} \tag{3.11}$$

Given the equality in Equation (3.11), followed by substitution from Equation (3.10) yields

$$E = \frac{1}{2}mv^2 - mv^2 = -\frac{e^2}{8\pi\varepsilon_0 r} \tag{3.12}$$

- *The quantum restriction postulate*: Only certain quantized orbits will be allowed. These orbits are restricted to the condition where the angular momentum (l) is an integral multiple of $h/2\pi$:

$$l = mvr = \frac{nh}{2\pi}, \quad \text{where } n = 1, 2, 3, \ldots \tag{3.13}$$

Solving Equation (3.12) for mvr and setting it equal to Equation (3.13) yields

$$mvr = \frac{e^2}{4\pi\varepsilon_0 v} = \frac{nh}{2\pi} \tag{3.14}$$

Solving Equation (3.14) for v and substituting for E in Equation (3.12) yields

$$v = \frac{2\pi e^2}{4\pi\varepsilon_0 nh} \tag{3.15}$$

$$E = -\frac{1}{2}mv^2 = -\frac{2\pi^2 me^4}{(4\pi\varepsilon_0)^2 n^2 h^2} \tag{3.16}$$

- When an electron jumps from a higher to a lower energy orbit, the energy difference (ΔE) will be emitted as a photon:

$$E = E_i - E_f = \frac{2\pi^2 me^4}{(4\pi\varepsilon_0)^2 h^2}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \tag{3.17}$$

Substituting e = 1.602×10^{-19} C, $m_e = 9.109 \times 10^{-31}$ kg, $4\pi\varepsilon_0 = 1.113 \times 10^{-10}$ $C^2/J{\cdot}m$, and $h = 6.626 \times 10^{-34}$ J·s, one obtains a value of 2.178×10^{-18} J for R_∞.

- It is impossible to describe the electron when it is in between the stationary state orbits.

Example 3-6. Prove that Equation (3.17) is just another way of stating the Rydberg formula given in Equation (3.9).

Solution. Combining Equation (3.17) with the Planck formula $\Delta E = h\nu$:

$$\frac{1}{\lambda} = \frac{\nu}{c} = \frac{\Delta E}{hc} = \frac{2.178 \times 10^{-18}\,\mathrm{J}}{(6.626 \times 10^{-34}\,\mathrm{J \cdot s})(2.998 \times 10^{8}\,\mathrm{m/s})}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

$$\frac{1}{\lambda} = 1.096 \times 10^{7}\,\frac{1}{\mathrm{m}}\left(\frac{1\,\mathrm{m}}{100\,\mathrm{cm}}\right) = 1.096 \times 10^{5}\,\mathrm{cm}^{-1}$$

This result is consistent with the Rydberg formula to the number of significant figures presented.

Using the circular orbits of the Bohr model, the meaning of the subscripts in the quantum numbers n_f and n_i now become obvious: n_i is the initial Bohr orbit (the one farther from the nucleus, or the excited state) and n_f is the final Bohr orbit, as shown in Figure 3.18. The following values of n_f correspond with the listed series: $n_f = 1$ (Lyman), $n_f = 2$ (Balmer), $n_f = 3$ (Paschen), $n_f = 4$ (Brackett), and $n_f = 5$ (Pfund). Thus, for example, the first four lines for the Balmer series originate in the $n_i = 3$, 4, 5, and 6 energy levels and terminate in the $n_f = 2$ level, as shown in Figure 3.18.

The actual radius of a Bohr orbit can be calculated by solving Equation (3.12) for r and substituting the value of E given by Equation (3.17), as shown in Equation (3.18). Defining the first Bohr radius ($n = 1$) as a_0, the other allowed orbital radii therefore go as $a_0\, n^2$, as shown in Figure 3.19.

$$r = -\frac{e^2}{8\pi\varepsilon_0 E} = \frac{4\pi\varepsilon_0 n^2 h^2}{4\pi^2 m e^2} \tag{3.18}$$

Example 3-7. Prove that $a_0 = 52.9$ pm.

Solution. According to Equation (3.18), $a_0 = \frac{(1.113\times10^{-10}\,\mathrm{C^2/Jm})(6.626\times10^{-34}\,\mathrm{J{\cdot}s})^2}{4(3.1416)^2(9.109\times10^{-31}\,\mathrm{kg})(1.602\times10^{-19}\,\mathrm{C})^2}$ $= 5.29 \times 10^{-11}$ m $= 52.9$ pm

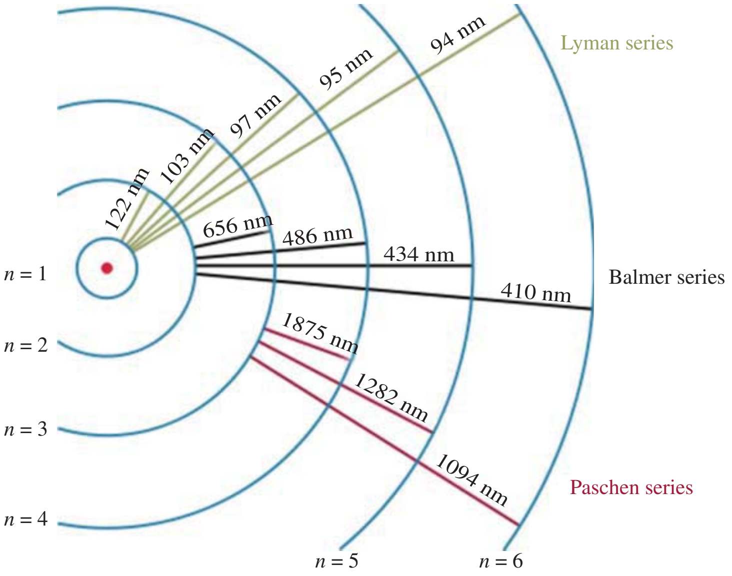


FIGURE 3.18
According to the Bohr model of the atom, the lines in the emission spectrum of hydrogen result from transitions between stationary orbits that exhibit quantization of angular momentum. The first several transitions and their corresponding wavelengths are shown for each series of lines in the line spectrum of hydrogen. [Attributed to Szdori, reproduced from http://en.wikipedia.org/wiki/Hydrogen_spectral_series (accessed November 30, 2013).]

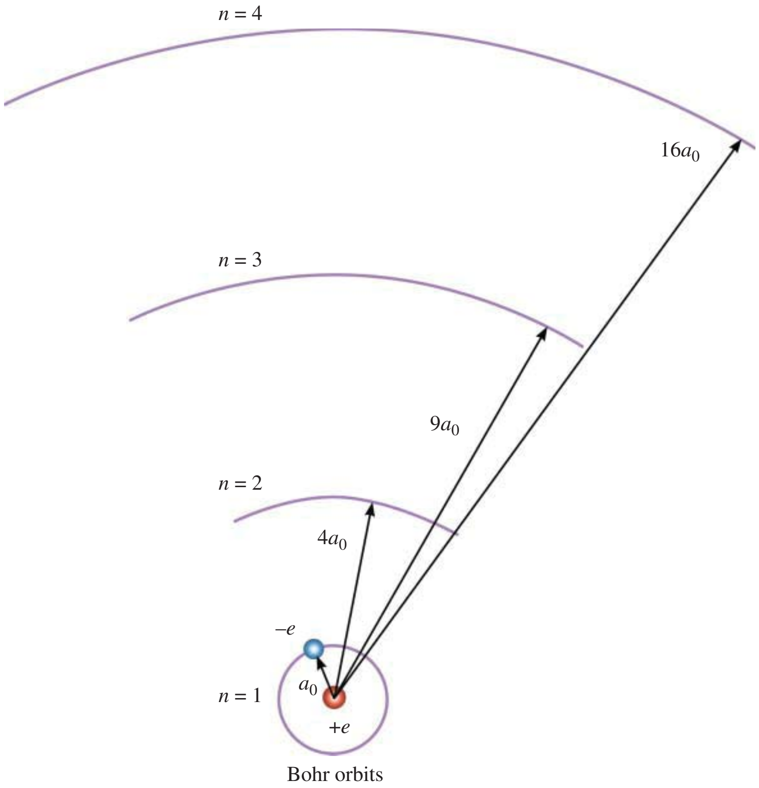


FIGURE 3.19
The allowed orbital radii in the Bohr model of the atom. [Blatt Communications.]

The Bohr model of the atom was well received by the scientific community. Although the theory could only explain the line spectrum of hydrogen and none of the other elements, it is nevertheless important because it was the first theoretical model of the atom to incorporate the concept of quantization. Various modifications were proposed by Sommerfeld and others in an attempt to reconcile the Bohr model with elements other than hydrogen. They did this by accounting for the fact that the electron and nucleus each revolve around a common center of mass, including a correction for the increased nuclear charge, and extending the theory to include elliptical orbits having a second quantum number. However, despite these improvements, the Bohr model could never fully explain the fine structure observed in the line spectra of certain elements. Although Bohr's stationary state and quantum restriction postulates flew right in the face of classical mechanics, the ultimate test of any revolutionary model is its ability to marry theory with experiment.

3.4 IMPLICATIONS OF WAVE-PARTICLE DUALITY

In 1924, the French aristocrat Louis de Broglie reasoned that if light can exhibit wave-particle duality, maybe matter can as well. By combining Einstein's equation for relativity (Eq. 3.19) with Planck's equation (Eq. 3.6), de Broglie derived the simple relationship in Equation (3.20). As the momentum is $p = mv$, de Broglie then generalized the result to include any free particle moving at any velocity v, instead of only photons. The *de Broglie relation*, as Equation (3.20) is called, predicted that matter (particularly electrons) might exhibit wavelike behavior. His thesis, entitled "Researches on the Quantum Theory," was reviewed by Einstein and was one of the shortest doctoral dissertations in history. The wave-particle duality of matter was so revolutionary that Nobel laureate Max von Laue was quoted as saying, “If that turns out to be true, I’ll quit physics.”

$$E = mc^2 \tag{3.19}$$

$$\lambda = \frac{hc}{E} = \frac{h}{mc} = \frac{h}{mv} = \frac{h}{p} \tag{3.20}$$

Nonetheless, experimental confirmation was not far behind. Only 2 years later, Davisson and Germer were the first to observe the wavelike properties of matter. Upon firing a beam of electrons at a nickel crystal, the researchers observed a diffraction pattern emerging from the other side of the crystal. Feynman likened the experiment to a modern-day double-slit experiment, where the bullets from a machine gun, fired one at a time through two closely spaced holes somehow managed to interfere with each other. The only plausible explanation was if one assumed that the electrons had wave-particle duality. Incidentally, Davisson shared the 1937 Nobel Prize in physics with George Paget Thomson, who independently discovered the phenomenon of electron diffraction. In one of the strangest ironies in the history of science, G. P. Thomson received the Nobel Prize for his experiments proving that the electron behaved like a wave, while his father J. J. Thomson won the 1906 Nobel Prize for proving that the electron was a particle. De Broglie won his own Nobel Prize in physics in 1929.

Example 3-8. Calculate the de Broglie wavelength of an electron traveling at one-tenth the speed of light. Do the same for a Nolan Ryan fastball traveling at 100 mph. Comment on the results.

Solution. The de Broglie wavelength of an electron can be calculated from Equation (3.20):

$$\lambda = \frac{h}{mv} = \frac{(6.626 \times 10^{-34}\ \mathrm{J \cdot s})}{(9.109 \times 10^{-31}\ \mathrm{kg})(2.998 \times 10^{8}\ \mathrm{m/s})} = 2.43 \times 10^{-11}\ \mathrm{m}$$

For a 142 g baseball traveling at roughly 100 mph:

$$v = \frac{100\ \mathrm{mi}}{\mathrm{h}}\left(\frac{1.609\ \mathrm{km}}{1\ \mathrm{mi}}\right)\left(\frac{10^3\ \mathrm{m}}{1\ \mathrm{km}}\right)\left(\frac{1\ \mathrm{h}}{3600\ \mathrm{s}}\right) = 44.7\ \mathrm{m/s}$$

$$\lambda = \frac{h}{mv} = \frac{(6.626 \times 10^{-34}\ \mathrm{J \cdot s})}{(0.142\ \mathrm{kg})(44.7\ \mathrm{m/s})} = 1.04 \times 10^{-34}\ \mathrm{m}$$

The wavelength of an electron is larger than its radius, while the wavelength of the baseball is insignificant compared with the size of the ball. Therefore, the wavelike nature of matter is only important for extremely small objects, such as atoms, nucleons, and electrons.

The de Broglie relation provided some additional footing for the quantum restriction postulate in the Bohr model of the atom. By assuming that the electron exhibits wavelike properties, only those circular orbits for which the circumference ($2\pi r$) is equal to an integral multiple of the wavelength ($n\lambda$) will form a standing wave, as shown in Figure 3.20. Thus, the quantization of angular momentum that Bohr applied in the third postulate (Eq. 3.13) of his derivation follows naturally from a wave-mechanical description of the electron, according to Equation (3.21). Hence, the allowed Bohr orbits can be considered circular standing waves, such as the ones depicted in this figure. The corresponding shapes of the vibrations shown in Figures 3.7 and 3.13 can be obtained by snipping each circular orbit

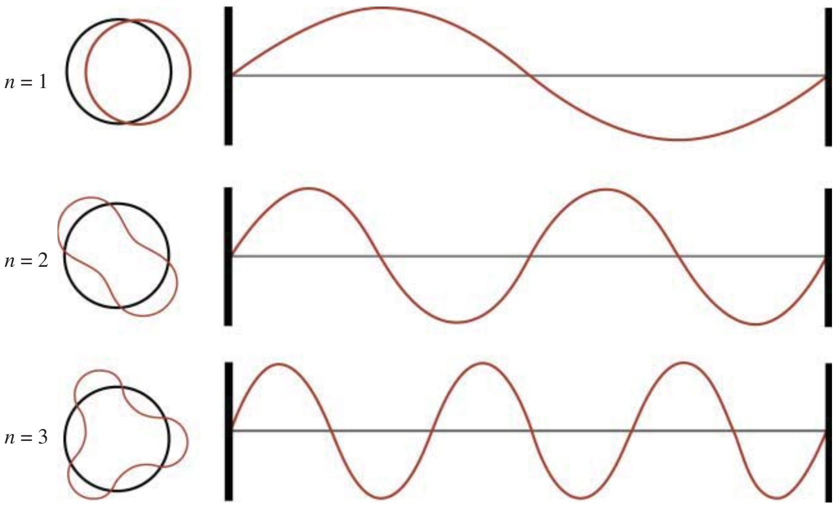


FIGURE 3.20
The first three (n = 1, 2, 3) de Broglie waves superimposed on the Bohr model of the atom. [Blatt Communications.]

and stretching the resulting string out between two fixed points in space. The wavelike properties of electrons form the basis of electron microscopes. Using these instruments, exceedingly short wavelengths of light can be used to probe the sample by controlling the velocity of the electron with an applied voltage.

$$2\pi r = n\lambda = \frac{nh}{mv}$$
$$l = mvr = \frac{nh}{2\pi} \tag{3.21}$$

In 1925, when he was only 23 years of age, Werner Heisenberg published his principle of indeterminacy, more commonly known as the *Heisenberg uncertainty principle*. According to the *Heisenberg uncertainty principle*, the wave-particle duality of matter places an inherent limitation on one's ability to simultaneously measure both the position and the momentum (and hence the velocity) of an electron. In order to precisely measure the position of an electron, one would need to bombard it with a photon having a very short wavelength. Because shorter wavelengths imply higher energies, the collision of the photon with the electron would impart a large uncertainty in the momentum of the electron. In mathematical terms, the result is expressed by Equation (3.22).

$$\Delta x \Delta p \geq \frac{h}{4\pi} \tag{3.22}$$

An appropriate analogy involves trying to photograph the headlights of a car in a busy intersection at night. If a very short shutter speed is used, the position of the car (or at least its leading edge) can be determined with a high degree of precision. However, any calculation of the car's momentum using this photograph will have a large amount of error. On the other hand, one can measure the car's momentum by using a longer shutter speed and holding the aperture of the camera open for a specified period of time. The resulting photograph will show a blurring of the headlights, so that their exact position cannot be ascertained. It is important to recognize that the Heisenberg principle has nothing at all to do with the limitations of the equipment—in this case, the camera. Rather, it is a fundamental property of the measurement itself.

Suppose that we were to add two sine waves having slightly different frequencies together. The two waves will constructively interfere with each other at certain

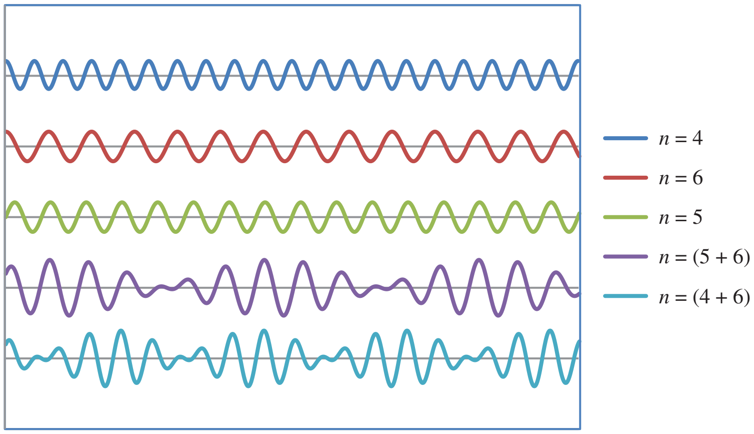


FIGURE 3.21
The addition of two (or more) standing waves leads to a beat pattern, where the width of the pulse is inversely related to the difference in frequencies used in the linear combination. The standing waves for $n = 4$, $n = 6$, and $n = 5$ are shown at the top of the illustration. Addition of the standing waves $n = 5$ and $n = 6$ yields a beat pattern having an uncertainty in x of 1.0, while addition of the standing waves $n = 4$ and $n = 6$ yields a beat pattern having an uncertainty in x of 0.5. In general, Δx for any superposition of two standing waves will be inversely proportional to Δn. Thus, in order to localize the wave function to a narrow region in space, the difference in energy between the standing waves in the superposition must increase, leading to a larger uncertainty in the momentum.

points in time and then destructively interfere at different times, creating what is known as a *beat pattern*, as shown in Figure 3.21.

The beat pattern consists of what is known as a *pilot wave* or a *wave packet*. As indicated in the diagram, one of the ways to localize the wave packet into a narrow region of space is to combine two waves that have vastly different wavenumbers (the wavenumber $1/\lambda$ is directly related to the momentum by a factor of h). Thus, in order to minimize the uncertainty in the position, a wider range of wavelengths (or a greater uncertainty in momentum) is required, as illustrated in Figure 3.22. This is simply a qualitative restatement of the Heisenberg uncertainty principle.

Further, it can be shown that the larger the number of sine waves added together, such that they are all arranged to be in phase with one another at time $t = 0$, the more defined the wave packet will become. As shown in Figure 3.23, the superposition of many sine waves produces a pulse of radiation having a measurable pulse width. Suppose that we add together a very large number of sine waves chosen from a distribution of frequencies that is $\pm 5\%$ of the center frequency υ_0, such that $\Delta\upsilon = \pm 0.05\upsilon_0$. If we define the uncertainty in time as the half-width at half-maximum of the wave packet, then the uncertainty for this particular group of sine waves will be $\Delta t = 5$, because about five cycles will occur within this timeframe (half the length of the arrow). Thus, the product of the uncertainties is given by Equation (3.23). Substitution of Equation (3.6) into Equation (3.23) yields

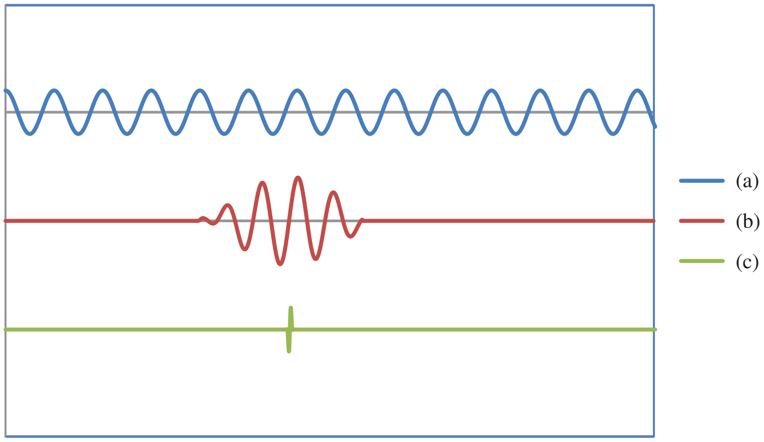


FIGURE 3.22
Illustration of the Heisenberg uncertainty principle for a wave packet. (a) A standing wave having $\Delta p_x \to 0$ has $\Delta x \to \infty$; (b) the superposition of standing waves having a nonzero but finite Δp_x has an intermediate value of Δx as the wave packet becomes defined in space; and (c) the superposition of standing waves where $\Delta p_x \to \infty$ causes $\Delta x \to 0$ and localizes the wave packet.

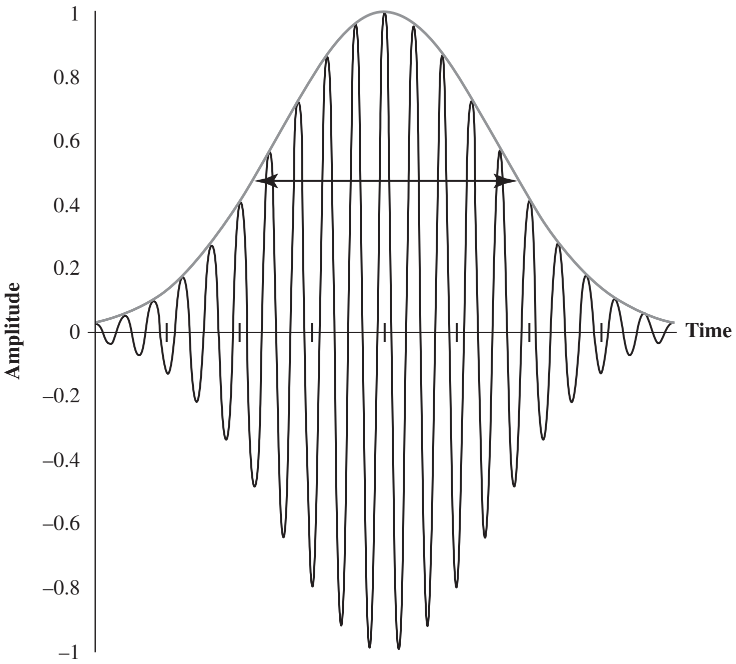


FIGURE 3.23
The superposition of a large number of sine waves having a distribution of frequencies such that $\Delta\upsilon = \pm 0.05\upsilon_0$. The arrow represents the full-width at half-maximum; half of its length represents the uncertainty in time of the wave packet. [Reproduced by permission from Warren, W. *The Physical Basis of Chemistry*, page 114, Copyright Elsevier (1994).]

Equation (3.24).

$$\Delta\nu\,\Delta t \geq 1/4 \tag{3.23}$$

$$\Delta E\,\Delta t \geq h/4 \tag{3.24}$$

Because the form of each sine wave was defined by Equation (3.4), the quantity x/λ must behave in the same manner as υt. Thus, $\Delta x\,\Delta(1/\lambda) \geq 1/4$. Finally, substitution of Equation (3.20) affords Equation (3.25), which is nearly identical to the Heisenberg uncertainty relationship in Equation (3.22), the main difference being in the exact manner in which the uncertainty is defined.

$$\Delta x\,\Delta p \geq h/4 \tag{3.25}$$

The Heisenberg uncertainty principle explains several interesting features of atoms. For instance, electrons cannot exist in planar orbits around the nucleus, as is so commonly depicted by the Bohr model of the atom. The reason for this is because in a planar orbit the uncertainty in position perpendicular to the plane is zero and therefore the momentum in that direction would become infinite. Likewise, the uncertainty principle can explain why the electron in a hydrogen atom does not collapse into the nucleus despite the fact that there is a strong electrostatic attraction in that direction. As the electron's orbit gets smaller, so does the uncertainty in its position. Therefore, the uncertainty in its momentum (and also in its kinetic energy) must necessarily increase.

The uncertainty principle can also be demonstrated using a modern-day version of Young's double-slit experiment. Consider that a beam of electrons is fired at a screen having two narrow slits. A suitable detector is placed some distance behind the screen in order to monitor the positions of the electrons. When one of the slits is closed, the electrons striking the detector form a Gaussian distribution exactly opposite the open slit, as might be expected. If this slit is then closed and the other one opened, a second Gaussian distribution appears at the detector opposite the

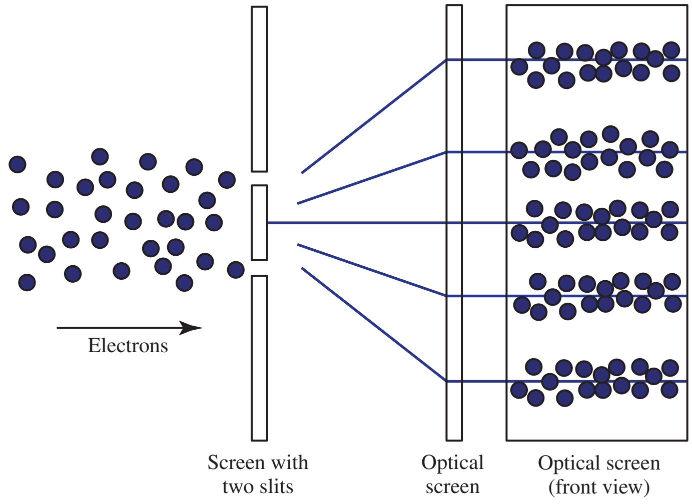


FIGURE 3.24
Modern-day version of the double-slit experiment using a beam of electrons. Even when the electrons are fired one at a time through the screen with the slits, an interference pattern develops on the optical screen. [Reproduced from http://commons.wikimedia.org /wiki/File:Two-Slit_Experiment_ Electrons.svg (accessed December 1, 2013).]

second slit. However, when a large number of electrons are fired at the screen with both of the slits open, instead of just the sum of two Gaussians, the detector records an interference pattern similar to the one shown in Figure 3.2. This is a remarkable observation in and of itself. Somehow the electrons passing through the two open slits have interfered with one another. Now suppose that the electron gun is modulated so that it releases just a single electron at a time. At first, the pattern observed at the detector appears completely random. But if we wait long enough for a larger number of electrons to pass through one or the other slit (*one at a time*), an astounding result is observed—the exact same interference pattern develops at the detector, as shown in Figure 3.24. The only conclusion that can be drawn is that the electron somehow interfered with itself as it passed through the barrier with the two slits in it.

The key to understanding this seeming paradox is put forward in the *superposition principle*, which is entirely a quantum mechanical concept. Consider the apparatus shown in Figure 3.25. A beam of photons enters from the left and strikes a beam splitter. Exactly one-half of the time the photon will be directed to the left along translation state 1 toward a mirror, while the other half of the time it will pass directly through the beam splitter along translation state 2. Regardless of the pathway, the total distance that the photon travels before it returns to the beam splitter and is sent to a detector is exactly the same. Furthermore, we can adjust the intensity of the light beam so that only one photon at a time will pass through

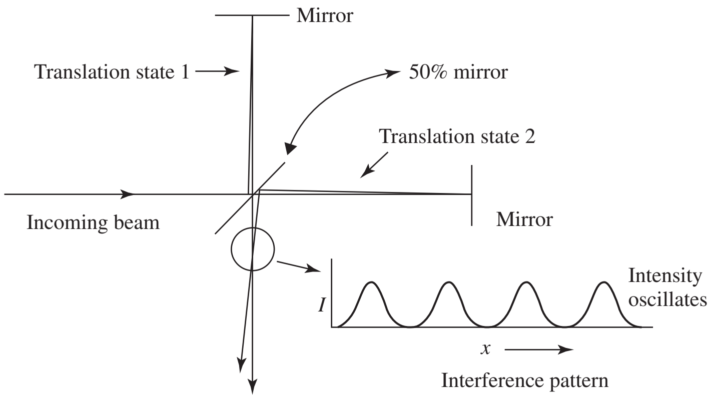


FIGURE 3.25
Schematic of an optical interference apparatus. [© Michael D Fayer, *Elements of Quantum Mechanics*, 2001, by permission of Oxford University Press, USA.]

the apparatus. Because there is only one photon in the apparatus at a time, there is no other photon with which to interfere. Nevertheless, an interference pattern is still observed at the detector.

The superposition principle (also known as *quantum entanglement*) states that whenever the photon is in one state, it can always be considered to be partly in *each* of the two states. In other words, the photon actually exists in an indeterminate state that is a linear combination of the two possible translational states, as shown by Equation (3.26). The probability of measuring result T_1 or T_2 in a *single measurement* depends on the relative weights of T_1 and T_2 in the superposition. The electrons in the modern-day double-slit experiment act as a superposition of the two different slits.

$$T = c_1 T_1 + c_2 T_2 \tag{3.26}$$

One of the most important ramifications of the uncertainty principle is that it brought about a radical change in the philosophy of science. Classical mechanics was deterministic in nature; that is to say that if the precise position and momentum of a particle or a collection of particles were known, Newton's laws could be used (at least in principle) to determine all the future behavior of the particle(s). The uncertainty principle, however, tells us that there is an inherent limitation to how accurately we can measure the two quantities simultaneously. Any observation of an extremely small object (one whose wavelength is on the same magnitude or larger than the particle itself) necessarily effects a nonnegligible disturbance to the system, and thereby it influences the results. Einstein never liked the statistical nature of quantum mechanics, saying "God does not play dice with the universe." Nonetheless, the quantum mechanical model is a statistical one.

It is for this reason that the Bohr model of the atom is correct only for one-electron systems such as hydrogen. For any multielectron system, such as helium, if we chose to focus on one electron and to calculate the electrostatic field that it felt as a result of its interactions with the nucleus and with the other electron, we would encounter a situation known as the *electron correlation problem*. While we might be able to locate the position of the other electron fairly precisely, because of the uncertainty in its momentum we would have no way of predicting its future behavior. The bottom line is that we no longer have a deterministic model of the atom. As strange as it might seem, given the inherent limitations of our observations, the best that we can do is to have a statistical view of the subatomic world. We can say, for instance, that there will be a 50% chance that the second electron will occupy a certain region of space. Hence, in the forthcoming discussion of quantum mechanics, we change our terminology from electron "orbits" to "orbitals," or regions of space where there is simply a strong likelihood of finding an electron. By virtue of its existence as a standing wave, the electron can exist "everywhere at once" (excluding the nodes) with a probability that is somehow related to its amplitude. If this sounds a little strange to you at this point, you are probably not alone. As Bohr himself once cautioned: "If quantum mechanics hasn't profoundly shocked you, you haven't understood it yet." So take a moment to ask yourself, "Are you profoundly shocked yet?"

3.5 POSTULATES OF QUANTUM MECHANICS

The quantum mechanical model of atomic structure is based on a set of postulates that can only be justified on the basis of their ability to rationalize experimental behavior. However, the foundations of quantum theory have their origins in the field of classical wave mechanics. The fundamental postulates are as follows:

- *Postulate 1*: The state of a particle is completely described by a wave function Ψ, such that all the possible information that can be measured about the particle (its position, momentum, energy, etc.) is contained in Ψ. The *Born interpretation* of the wave function, which itself derives from the fact that the intensity of light is proportional to the square of its amplitude, states that $\Psi^*\Psi$ represents the *probability density* that the particle will exist in the volume element $d\tau$ at point (x, y, z). Recall that the Heisenberg uncertainty principle states that we cannot measure the exact position of the particle—only a statistical probability can be obtained. The quantity Ψ^* is the complex conjugate of the wave function Ψ. Thus, for example, if Ψ is the complex function $x + iy$, Ψ^* will equal $x - iy$. The derivative $\partial\tau$ is an infinitely small, three-dimensional volume element. Because $\Psi^*\Psi$ represents a probability density, Ψ and Ψ^* must both be single-valued, continuous, finite, and smoothly varying. Furthermore, the integral of $\Psi^*\Psi$ over all space must be unity, as shown in Equation (3.27), because the total probability of finding the particle somewhere has to be 100%. Wave functions that satisfy Equation (3.27) are said to be *normalized*.

$$\int_{-\infty}^{\infty} \Psi^*\Psi \, \partial\tau = 1 \tag{3.27}$$

- *Postulate 2*: For every physically observable variable in classical mechanics, there exists a corresponding linear, Hermitian operator in quantum mechanics. Examples are shown in Table 3.2, where the ^ symbol indicates a quantum mechanical operator and $\hbar = h/2\pi$. A *Hermitian operator* is one which satisfies Equation (3.28).

$$\int \Psi_i{}^*\widehat{A}\Psi_j\partial\tau = \int \Psi j^*\widehat{A}\Psi_i \, \partial\tau \tag{3.28}$$

Many quantum mechanical operators will define an eigenvalue equation. An *eigenfunction* is any function that when operated on yields back the original function times a constant. That constant is known as the *eigenvalue*. The requirement that each operator be Hermitian therefore guarantees that the eigenvalues will always be real numbers. Any two eigenfunctions that have the same eigenvalue are said to be *degenerate* and will possess the same energy. As a result of the requirement that quantum mechanical operators be linear, any linear combination of degenerate wave functions will also be an acceptable solution. Furthermore, any well-behaved function (one subject to the same restrictions as Ψ was in Postulate 1) can be expanded as a linear combination of eigenfunctions. This property is analogous to the superposition of standing waves. Eigenfunctions that are not degenerate will be *orthogonal* to each other, according to Equation (3.29).

$$\int \Psi_i{}^*\Psi_j\partial\tau = 0, \quad i \neq j \tag{3.29}$$

- *Postulate 3*: In any measurement where an exact solution can be obtained, the only values that will ever be observed are the eigenvalues a_n that satisfy the eigenvalue equation given by Equation (3.30). This postulate is the one that is responsible for the quantization of energy.

$$\widehat{A}\Psi_n = a_n\Psi_n \tag{3.30}$$

Although measurements must always yield an eigenvalue, the state does not initially have to be an eigenstate of $\widehat{A}$. Any arbitrary state can be expanded

TABLE 3.2 Classical mechanical observables and their quantum mechanical operators.

Observable		Operator	
Type	Symbol	Symbol	Operation
Position	x	$\hat{X}$	Multiply by x
Position vector	$\mathbf{r}$	$\hat{R}$	Multiply by r
Momentum	p_x	$\hat{P}$	$-i\hbar\frac{\partial}{\partial x}$
Momentum vector	$\mathbf{p}$	$\hat{P}$	$-i\hbar\left(\mathbf{i}\frac{\partial}{\partial x}+\mathbf{j}\frac{\partial}{\partial y}+\mathbf{k}\frac{\partial}{\partial z}\right)$
Kinetic energy	K_x	$\hat{K}_x$	$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$
	K	$\hat{K}$	$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)$ $=-\frac{\hbar^2}{2m}\nabla^2$
Potential energy	$V(x)$	$\hat{V}(x)$	Multiply by $V(x)$
	$V(x,y,z)$	$\hat{V}(x,y,z)$	Multiply by $V(x,y,z)$
Total energy	E	$\hat{H}$	$-\frac{\hbar^2}{2m}\nabla^2+V(x,y,z)$
Angular momentum	L_x	$\hat{L}_x$	$=-i\hbar\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)$
	L_y	$\hat{L}_y$	$=-i\hbar\left(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z}\right)$
	L_z	$\hat{L}_z$	$=-i\hbar\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)$

as a linear combination in the complete set of eigenfunctions, as shown in Equation (3.31).

$$\Psi = \sum_{i}^{n} c_i \Psi_i \tag{3.31}$$

- *Postulate 4*: If Ψ is not an eigenfunction of the quantum mechanical operator, then a series of measurements on identical systems of particles will yield a distribution of results, such that Equation (3.32) will describe the average (or "expectation") value of the observable (assuming the wave function is normalized).

$$< a >= \int_{-\infty}^{\infty} \Psi^* \hat{A} \Psi \, \partial\tau \tag{3.32}$$

- *Postulate 5*: The wave function of a particle evolves in time according to the time-dependent Schrödinger equation, given by Equation (3.33).

$$-\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi = \hat{H}\Psi = -i\hbar\frac{\partial\Psi}{\partial t} \tag{3.33}$$

3.6 THE SCHRÖDINGER EQUATION

Quantum mechanics is a model that is based entirely on postulates that explain the observations associated with atomic and subatomic particles. As such, the Schrödinger equation cannot be derived from first principles. However, what follows is a rationale for the Schrödinger equation. The classical wave equation in one-dimension was given by Equation (3.3) and is reproduced in Equation (3.34) with the substitution of Ψ for y.

$$\frac{\partial^2\Psi}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2\Psi}{\partial t^2} \tag{3.34}$$

A general solution to the Schrödinger equation is given by Equation (3.35).

$$\Psi(x,t) = A\,e^{2\pi i\left(\frac{x}{\lambda}-\nu t\right)} \tag{3.35}$$

Example 3-9. Prove that Equation (3.35) is a solution to Equation (3.34).

Solution. Taking the first partial derivative of Ψ with respect to x and t gives the following two equations:

$$\frac{\partial\Psi}{\partial x} = \frac{2\pi i}{\lambda}Ae^{2\pi i\left(\frac{x}{\lambda}-\nu t\right)}$$

$$\frac{\partial\Psi}{\partial t} = -2\pi i\nu Ae^{2\pi i\left(\frac{x}{\lambda}-\nu t\right)}$$

Taking the second partial derivative with respect to each independent variable yields

$$\frac{\partial^2\Psi}{\partial x^2} = -\left(\frac{2\pi}{\lambda}\right)^2 Ae^{2\pi i\left(\frac{x}{\lambda}-\nu t\right)} = -\left(\frac{2\pi}{\lambda}\right)^2\Psi$$

$$\frac{\partial^2\Psi}{\partial t^2} = -(2\pi\nu)^2Ae^{2\pi i\left(\frac{x}{\lambda}-\nu t\right)} = -(2\pi\nu)^2\,\Psi$$

After substituting into Equation (3.34):

$$-\left(\frac{2\pi}{\lambda}\right)^2\Psi = -\frac{(2\pi\nu)^2}{v^2}\Psi$$

which yields the following after taking the square root of both sides and cancelling:

$$\frac{1}{\lambda} = \frac{\nu}{v}$$

Because this is just a reformulation of Equation (3.1), Equation (3.35) is an acceptable solution to Equation (3.34). In fact, it is the most general solution.

Substituting the de Broglie relation given by Equation (3.20) into the second partial derivative of Equation (3.35) with respect to x yields Equation (3.36).

$$\frac{\partial^2\Psi}{\partial x^2} = -\frac{4\pi^2}{\lambda^2}\Psi = -\frac{4\pi^2m^2v^2}{h^2}\Psi \tag{3.36}$$

Given that the kinetic energy $K = (1/2)mv^2$ and the total energy $E = K + V$, where V is the potential energy, Equation (3.36) can be rewritten as

$$\frac{\partial^2\Psi}{\partial x^2} = -\frac{8\pi^2 mK}{h^2}\Psi = -\frac{8\pi^2 m}{h^2}(E\Psi - V\Psi) \tag{3.37}$$

Solving for the first partial derivative of Equation (3.35) with respect to time and substituting the Planck formula $E = h\nu$, we obtain Equation (3.38):

$$\frac{\partial\Psi}{\partial t} = -2\pi i\nu\Psi = -\frac{2\pi iE}{h}\Psi \tag{3.38}$$

Solving both Equations (3.37) and (3.38) for $E\Psi$ and setting them equal yields Equation (3.39):

$$E\Psi = -\frac{h^2}{8\pi^2 m}\frac{\partial^2\Psi}{\partial x^2} + V\Psi = -\frac{h}{2\pi i}\frac{\partial\Psi}{\partial t}\left(\frac{i}{i}\right) = \frac{ih}{2\pi}\frac{\partial\Psi}{\partial t} \tag{3.39}$$

Finally, some simple rearrangement yields the time-dependent Schrödinger equation in one-dimension, given by Equation (3.40).

$$-\frac{h^2}{8\pi^2 m}\frac{\partial^2\Psi}{\partial x^2} + V\Psi = \frac{ih}{2\pi}\frac{\partial\Psi}{\partial t} \tag{3.40}$$

Generalizing from one-dimension to three-dimensions and substituting del-squared as the operator yields Equation (3.41), the time-dependent Schrödinger equation in three-dimensions, which is the same as Equation (3.33).

$$-\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi = H\Psi = i\hbar\frac{\partial\Psi}{\partial t},$$
$$\text{where } \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{3.41}$$

For stationary states, analogous to Bohr's stationary orbits where the potential energy is independent of time, $\Psi(x, y, z, t)$ can be factored into a time-dependent term $\phi(t)$ and a time-independent term $\psi(x, y, z)$, as shown in Equation (3.42).

$$\Psi(x,y,z,t) = \psi(x,y,z)\,\phi(t) \tag{3.42}$$

Taking Equation (3.41) and dividing both sides by $\psi\phi$ yields Equation (3.43).

$$-\frac{\hbar^2}{2m}\frac{\nabla^2\psi\phi}{\psi\phi} + \frac{V\psi\phi}{\psi\phi} = i\hbar\frac{\psi}{\psi\phi}\frac{\mathrm{d}\phi}{\mathrm{d}t} \tag{3.43}$$

Because the del-squared operator acts only on position coordinates, both it and the potential energy term on the left-hand side of Equation (3.43) are independent of time and the $\phi(t)$s cancel on this side. Likewise, because the operator on the right-hand side of Equation (3.43) is independent of the coordinates, the $\psi(x, y, z)$s cancel on the right-hand side. Setting both sides equal to the separation constant (a scalar quantity) yields Equation (3.44).

$$-\frac{\hbar^2}{2m}\frac{\nabla^2\psi}{\psi} + \frac{V\psi}{\psi} = \frac{i\hbar}{\phi}\frac{\mathrm{d}\phi}{\mathrm{d}t} = E \tag{3.44}$$

Rearrangement of Equation (3.44) and substitution of the symbol for the Hamiltonian operator yields the familiar time-independent form of the Schrödinger equation shown in Equation (3.45).

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = \widehat{H}\psi = E\psi = \frac{i\hbar}{\phi}\frac{d\phi}{dt} \tag{3.45}$$

The time-independent Schrödinger equation in one-dimension is a linear, second-order differential equation having constant coefficients. A general method for solving this type of differential equation is to rearrange the equation into a quadratic of the form shown in Equation (3.46), where y'' and y' are the second and first derivatives, respectively, with respect to x.

$$y'' + py' + qy = 0 \tag{3.46}$$

Because we are looking for a function whose first and second derivatives yield back the function times a constant, one logical solution would be an exponential function, such as $y = e^{sx}$. In this case, $y' = se^{sx}$ and $y'' = s^2e^{sx}$, so that substitution into Equation (3.46) yields Equation (3.47). When both sides of Equation (3.47) are divided by e^{sx}, the result is known as the *auxiliary equation* and is shown in (3.44).

$$s^2e^{sx} + pse^{sx} + qe^{sx} = 0 \tag{3.47}$$

$$s^2 + ps + q = 0 \tag{3.48}$$

Because Equation (3.48) is a quadratic, there are two independent solutions to the auxiliary equation. Thus, the most general solution to the differential equation given by Equation (3.46) is a linear combination, as shown in Equation (3.49), where a and b are weighting constants.

$$y(x) = a\,e^{s_1x} + b\,e^{s_2x} \tag{3.49}$$

In this context, the one-dimensional Schrödinger equation can be rewritten as Equation (3.50).

$$\frac{d^2\psi}{dx^2} + \frac{2m(E-V)\psi}{\hbar^2} = \frac{d^2\psi}{dx^2} + \beta^2\psi = 0 \tag{3.50}$$

After substitution, the auxiliary equation becomes:

$$(s^2 + \beta^2) = 0 \tag{3.51}$$

Therefore, $s^2 = -\beta^2$, or $s = \pm i\beta$ and the general solution to time-independent Schrödinger equation is given by Equation (3.52).

$$\psi(x) = a\,e^{i\beta x} + b\,e^{-i\beta x} \tag{3.52}$$

Using Euler's formula that $e^{i\beta x} = \cos(\beta x) + i\sin(\beta x)$, an alternative form of Equation (3.52) is Equation (3.53).

$$\psi(x) = A\,\cos(\beta x) + \ \ B\,\sin(\beta x) \tag{3.53}$$

Whether it is more convenient to use the exponential form given in Equation (3.52) or the trigonometric form given in Equation (3.53) will depend on the specific nature of the problem at hand.

One final point about wave functions is the requirement that they be normalized. Depending on the particular problem, the solution to Equation (3.53) might yield an eigenfunction where the integral of $\psi^*\psi$ dτ over all space is not equal to one. In this case, an appropriate constant c must be found such that the wave function can be normalized. The normalization process is shown in Equations (3.54)–(3.56).

$$\int_{-\infty}^{\infty} \psi^*\psi \, \partial\tau = \int_{-\infty}^{\infty} |\psi|^2 \partial\tau = N \tag{3.54}$$

$$\int_{-\infty}^{\infty} |c\psi|^2 \partial\tau = c^2 N = 1 \tag{3.55}$$

$$c = 1/\sqrt{N} \tag{3.56}$$

3.7 THE PARTICLE IN A BOX PROBLEM

Ultimately, our goal is to solve the Schrödinger equation in three-dimensions for the electron in the hydrogen atom. This electron is subject to a potential energy term that involves a Coulombic attraction toward the nucleus. However, the solution to this differential equation is not a trivial one. We therefore choose a somewhat similar, but simpler, problem—the particle in a box—to demonstrate the procedure and to illustrate some of the principles of quantum mechanics. We then extrapolate those results to the hydrogen atom in a later chapter.

Consider an electron that is trapped in a one-dimensional box of length a, such as the one shown in Figure 3.26. Inside the box, the electron experiences zero potential energy. However, the walls of the box are infinitely steep, so that the potential energy of an electron is infinite outside the box.

The wave function is zero everywhere outside the box. Inside the box, the time-independent Schrödinger equation in one-dimension reduces to Equation (3.57), which has the trigonometric solution given by Equation (3.53), where $\beta = \sqrt{2mE}/\hbar$.

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}E\psi = 0 \tag{3.57}$$

The boundary conditions are such that the wave function approaches zero at both walls of the box. In other words, $\psi(0) = \psi(a) = 0$. The condition that $\psi(0) = 0$ implies that $A = 0$, because $B\sin(0) = 0$. The condition that $\psi(a) = 0$ therefore implies that $B\sin(\beta a) = 0$. There are two conditions under which this will be true: if $B = 0$ or if $\sin(\beta a) = 0$. If $B = 0$, then the wave function would never exist, because A is also zero. Therefore, $\sin(\beta a)$ must equal zero; and this will only be true when $\beta a = n\pi$, where n is any integer. Solving Equation (3.58) for the energy yields the results given by Equation (3.59). Because the energy must always be greater than or equal to zero, n must equal a non-negative integer. Furthermore, if $n = 0$, E would also equal zero, and the two roots of the auxiliary equation would be identical. Thus, $n = 0$ is not an acceptable solution and the quantum number, n, must take on a positive value.

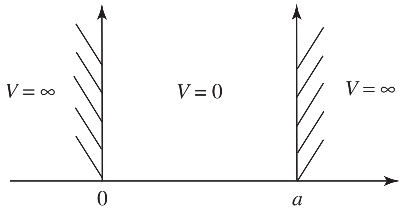


FIGURE 3.26
Sketch of the one-dimensional particle in a box problem.

After substitution for A and β into Equation (3.53), the acceptable solutions to the particle in a box problem are given in Equation (3.60).

$$\beta = \frac{\sqrt{2mE}}{\hbar} = \frac{n\pi}{a} \tag{3.58}$$

$$E = \frac{n^2\hbar^2\pi^2}{2ma^2} = \frac{n^2h^2}{8ma^2}, \quad \text{where } n = 1,\ 2,\ 3,\ \ldots \tag{3.59}$$

$$\psi(x) = B\ \sin\left(\frac{n\pi x}{a}\right) \tag{3.60}$$

Example 3-10. Use the normalization procedure discussed in the previous section to prove that the value of B in Equation (3.60) is $(2/a)^{1/2}$.

Solution. In the process of normalization, the integral of $|\psi|^2\, d\tau$ over all space is determined to be N. By substitution of Equation (3.60) for ψ, the following integral must be evaluated:

$$B^2 \int_0^a \sin^2\left(\frac{n\pi x}{a}\right) dx = N$$

Consultation of an integral table yields the following analytic solution:

$$\int_0^a \sin^2(kx)\, dx = \frac{a}{2} - \frac{1}{4k}\sin(2ka)$$

Because $\sin(2kx) = \sin(2n\pi x/a) = \sin(n'\pi) = 0$ for all n', the original integral reduces to $B^2\ (a/2) = N$. Because N must equal 1 in order for the wave function in Equation (2.60) to be normalized, B must therefore equal $(2/a)^{1/2}$. Thus, the normalized solutions to the one-dimensional particle in a box problem are

$$\psi(x) = \sqrt{\frac{2}{a}}\ \sin\left(\frac{n\pi x}{a}\right)$$

The acceptable solutions to the one-dimensional particle in a box problem are sketched in Figure 3.27(a) for the first several quantum numbers. The *Born interpretation* of the wave function states that the product $\psi^*\psi$ represents the probability density of finding the electron in a finite region of space. Because the Born interpretation of the wave function is $|\psi|^2$, this function is shown in Figure 3.27(b).

Three features are immediately evident:

1. The energy is quantized and it increases as the square of n.
2. For all $n > 1$, there are $n-1$ nodal regions of space where there is zero probability that the electron will exist.
3. When n is infinite, the shape of the wave function approaches that of a straight line. The peaks and valleys of the standing wave all blur together into a single continuum. Hence, the quantum mechanical model approximates the classical one at very large values of n, a property which is known as the *correspondence principle*. In order for any new theory of the atom to be valid, it must not only explain and predict new behavior but it must also incorporate all the experimental evidence that preceded it.

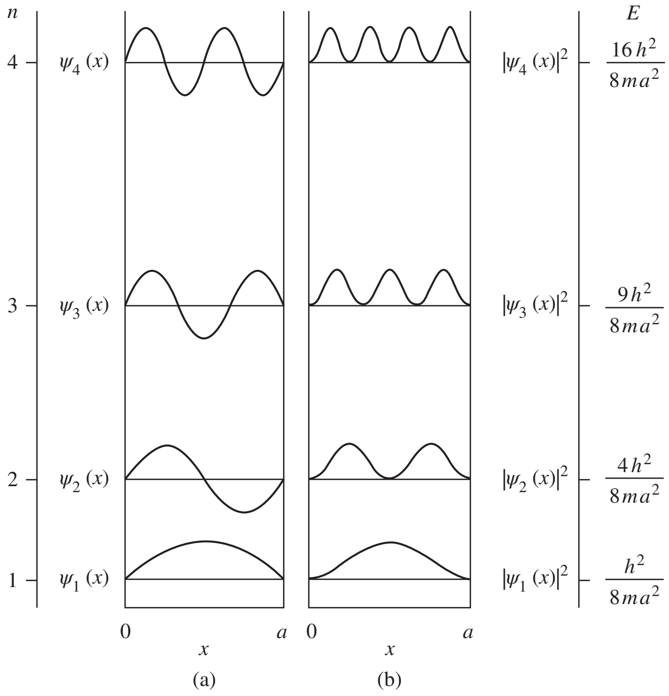


FIGURE 3.27

The first of several solutions to the particle in a box problem showing (a) $\psi(x)$ and (b) $|\psi(x)|^2$, along with their corresponding energies. [Copyright University Science Books, Mill Valley, CA. Used with permission. All rights reserved. McQuarrie, D. A.; Simon, J. D. Physical Chemistry: A Molecular Approach, 1997.]

Example 3-11. Prove that $\psi(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$ is an acceptable solution to the Schrödinger equation.

Solution. The time-independent Schrödinger equation in one-dimension is given by Equation (3.45):

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V\psi = \widehat{H}\psi = E\psi$$

Taking the first and second derivatives of Equation (3.45) yields

$$\frac{d\psi}{dx} = \left(\frac{n\pi}{a}\right)\sqrt{\frac{2}{a}}\cos\left(\frac{n\pi x}{a}\right)$$

$$\frac{d^2\psi}{dx^2} = -\left(\frac{n\pi}{a}\right)^2\sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right) = -\frac{n^2\pi^2}{a^2}\psi$$

Because $V = 0$ inside the box, substitution of the second derivative into the Schrödinger equation yields

$$-\frac{\hbar^2}{2m}\frac{n^2\pi^2}{a^2}\psi = E\psi$$

Substitution for $\hbar$ and division of both sides by ψ gives the expected result:

$$E = \frac{n^2h^2}{8ma^2}$$

Example 3-12. Using Postulate 4, show that the average position <*x*> of the electron in the one-dimensional particle in a box problem lies exactly in the center of the box.

Solution. The expectation value of position, <*x*> is given by Equation (3.32):

$$\langle x \rangle = \int_0^a \psi * x\psi \, \mathrm{d}\tau = \frac{2}{a}\int_0^a x \sin^2\left(\frac{n\pi x}{a}\right) \mathrm{d}x$$

Using a table of integrals:

$$\int_0^x x \sin^2(kx)\mathrm{d}x = \frac{x^2}{4} - \frac{x\ \sin(2kx)}{4k} - \frac{\cos(2kx)}{8k^2}$$

Because $k = n\pi/a$, $\sin(2ka) = \sin(2n\pi) = \sin(0) = 0$ and $\cos(2ka) = \cos(2n\pi) = \cos(0) = 1$. Therefore, the integrand reduces to

$$\int_0^x x \sin^2(kx)\mathrm{d}x = \frac{x^2}{4} - \frac{1}{8k^2} - \left(\frac{0}{4} - \frac{1}{8k^2}\right) = \frac{a^2}{4}$$

Substitution into the expectation value for *x* yields

$$\langle x \rangle = \frac{2}{a}\left(\frac{a^2}{4}\right) = \frac{a}{2} \text{ or in the exact middle of the box}$$

Because the hydrogen atom is a three-dimensional problem, let us next consider what happens when the particle is confined to a rectangular parallelepiped having the dimensions *a*, *b*, and *c*, as shown in Figure 3.28.

Inside the box, where the potential energy is zero, the time-independent Schrödinger equation in three-dimension is given by Equation (3.45). Separation of the variables yields Equation (3.61):

$$\psi(x, y, z) = X(x)\ Y(y)\ Z(z) \tag{3.61}$$

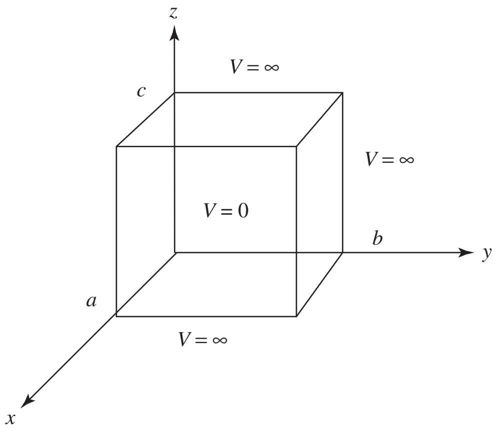


FIGURE 3.28
The particle in a three-dimensional box problem, where the box has dimensions of *a*, *b*, and *c*.

Substitution into Equation (3.45), followed by division by $X(x)Y(y)Z(z)$ gives Equation (3.62):

$$-\frac{\hbar^2}{2m}\frac{1}{X(x)}\frac{d^2X}{dx^2}-\frac{\hbar^2}{2m}\frac{1}{Y(y)}\frac{d^2Y}{dy^2}\frac{\hbar^2}{2m}\frac{1}{Z(z)}\frac{d^2Z}{dz^2}=E \tag{3.62}$$

Because each term on the left-hand side of Equation (3.62) is a function of a single variable, all three terms must be equal to a constant in order for the equation to be true at all values of x, y, and z. Thus, Equation (3.62) can be simplified as Equation (3.63):

$$E_x + E_y + E_z = E \tag{3.63}$$

The boundary conditions are $X(0) = X(a) = Y(0) = Y(b) = Z(0) = Z(c) = 0$. Each term in Equation (3.62) therefore reduces to the same form as the particle in a one-dimensional box, such that Equations (3.64) and (3.65) result:

$$\psi(x,\ y,\ z) = A\sin\left(\frac{n\pi x}{a}\right)B\sin\left(\frac{n\pi x}{b}\right)C\sin\left(\frac{n\pi x}{c}\right) \tag{3.64}$$

$$E = \frac{\hbar^2}{2m}\left(\frac{n_x^2}{a^2}+\frac{n_y^2}{b^2}+\frac{n_z^2}{c^2}\right) \tag{3.65}$$

Normalization of Equation (3.65) yields a value of $(8/abc)^{1/2}$ for the conglomerate constant ABC.

The first several energy levels for the three-dimensional particle in a box problem (where $a = b = c$) are shown in Figure 3.29, where the energy axis has units of $h^2/8\ ma^2$. Many of the energy levels are degenerate—having more than one acceptable set of quantum numbers at the same energy. For example, there are three ways to have the sum ${n_x}^2 + {n_y}^2 + {n_z}^2 = 6$: n_x, n_y, n_z = 2, 1, 1; 1, 2, 1; and 1, 1, 2. As a result, all three wave functions will have the same energy, where the $E = 6(h^2/8\ ma^2)$ energy level is said to be triply degenerate. The degeneracy is removed, however, if the symmetry of the box is lowered, so that it is no longer a cube: $a \neq b \neq c$. Consider the case where $b = (1/a)^{1/2}$ and $c = (1/a)^{1/3}$. The energies of the 2, 1, 1; 1, 2, 1; and 1, 1, 2 sets of quantum numbers are now $7(h^2/8\ ma^2)$, $8(h^2/8\ ma^2)$, and $9(h^2/8\ ma^2)$. This is the first of many examples in this textbook where we will find that the symmetry of an object greatly influences its physical and chemical properties.

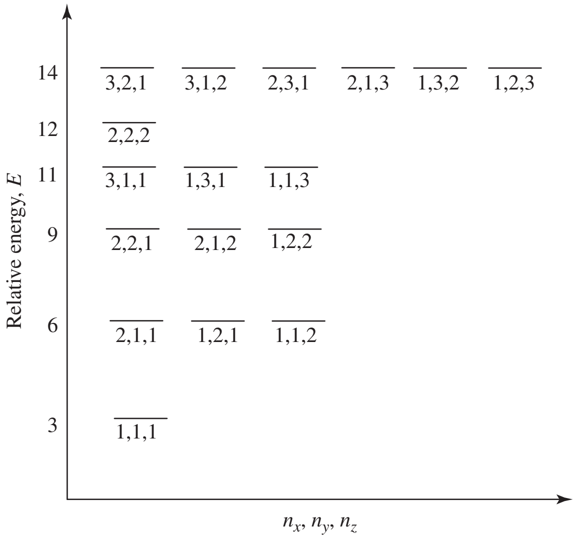


FIGURE 3.29
The relative energies (in units of $h^2/8\ ma^2$) for the three-dimensional particle in a box having sides with lengths $a = b = c$. The energy level labels list the three quantum numbers n_x, n_y, and n_z in that order. Notice that many of the energy levels are degenerate.

3.8 THE HARMONIC OSCILLATOR PROBLEM

A second common problem that occurs in chemistry is given by the harmonic oscillator model. Consider a block of mass *m* attached to a spring, as shown in Figure 3.30. If the other end of the spring is attached to a fixed point and the mass is displaced from its equilibrium position, its motion will oscillate in time. The harmonic oscillator problem is important in quantum chemistry because, to a certain extent, it models the behavior of nucleons in the nucleus, the motions of atoms in metallic solids, and the vibrations in polyatomic molecules. The periodic behavior of a harmonic oscillator can also be described by the angular motion of a pendulum swinging in the *xy* plane, as shown in Figure 3.31. The pendulum swings through an arc of length θ with an angular velocity ω that is equal to 2π radians/sec, such that Equation (3.66) describes the relationship between frequency and the angular velocity.

$$v = \frac{2\pi}{\omega} \tag{3.66}$$

Using Hooke's law, the restoring force for the mass on the spring in Figure 3.30 is given by Equation (3.67). Taking the integral of the force with respect to position yields the potential energy in Equation (3.68). Setting the force equal to Newton's second law yields Equation (3.69), which rearranged becomes Equation (3.70). This is a second-order differential equation with constant coefficients and it can therefore

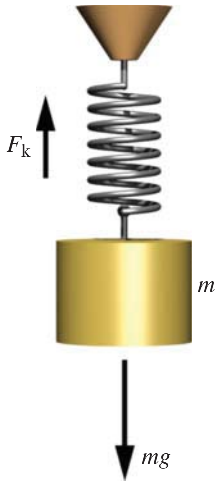


FIGURE 3.30
Harmonic oscillator model employing a mass m affixed to a spring having a force constant k. [Attributed to Svjo, reproduced from http://en.wikipedia.org/wiki/Hooke's_law (accessed December 1, 2013).]

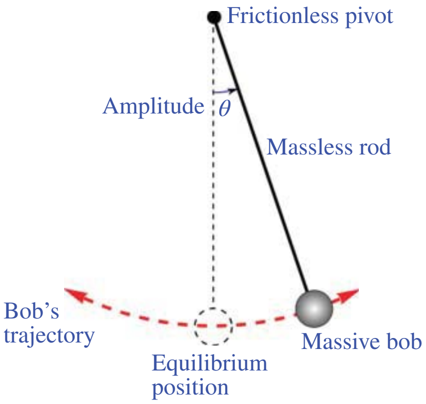


FIGURE 3.31
Harmonic motion of a pendulum. [Reproduced from http://en.wikipedia.org/wiki/Pendulum (accessed Decemebr 1, 2013).]

be solved using the auxiliary equation method described in the previous section. The general solution to Equation (3.70) in trigonometric form is given by Equation (3.53). The boundary condition that $x(0) = L$, where L is the maximum distance that the mass was stretched from its equilibrium position implies that the second term in Equation (3.53) is zero and $A = L$ and therefore the solution to Equation (3.70) reduces to Equation (3.71).

$$F = -kx \tag{3.67}$$

$$V(x) = -\int F\mathrm{d}x = -\int kx\mathrm{d}x = \frac{1}{2}kx^2 \tag{3.68}$$

$$F(x) = -kx = m\frac{\mathrm{d}^2x}{\mathrm{d}t^2} \tag{3.69}$$

$$\frac{\mathrm{d}^2x}{\mathrm{d}t^2} + \frac{k}{mx} = 0 \tag{3.70}$$

$$x(t) = A\cos(\beta t) = L\cos(\omega t),$$

$$\text{where } \omega = \sqrt{\frac{k}{m}} \tag{3.71}$$

Substituting the classical potential energy into the Schrödinger equation in one-dimension gives Equation (3.72). Following rearrangement and substitution of $\omega^2 = \mathrm{k/m}$, Equation (3.73) results.

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \frac{1}{2}kx^2\psi = E\psi \tag{3.72}$$

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \left(\frac{2mE}{\hbar^2} - \frac{\omega^2m^2x^2}{\hbar^2}\right)\psi = 0 \tag{3.73}$$

This second-order differential equation does not have constant coefficients (because of the x^2 term) and it cannot be solved in the same manner as Equation (3.57) using the auxiliary equation method. The solutions to the quantum harmonic oscillator problem are not trivial and will be presented here without proof. For a rigorous, but lucid, description of the calculus involved in solving Equation (3.73), the interested reader is referred to Fayer's *Elements of Quantum Mechanics*. The first few solutions, which are based on Hermite polynomials, are given by Equations (3.74)–(3.77), where $\alpha = m\omega/\hbar$, $y = \sqrt{\alpha}x$, and graphs of the corresponding wave functions are shown in Figure 3.32.

$$\Psi_0 = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-y^2/2} \tag{3.74}$$

$$\Psi_1 = \left(\frac{\alpha}{\pi}\right)^{1/4} \sqrt{2}y\, e^{-y^2/2} \tag{3.75}$$

$$\Psi_2 = \left(\frac{\alpha}{\pi}\right)^{1/4} \frac{1}{\sqrt{2}}(2y^2 - 1)e^{-y^2/2} \tag{3.76}$$

$$\Psi_3 = \left(\frac{\alpha}{\pi}\right)^{1/4} \frac{1}{\sqrt{3}}(2y^3 - 3y)\, e^{-y^2/2} \tag{3.77}$$

There are several very important features to note in Figure 3.32. First of all, according to classical mechanics, the mass on the end of the spring can have any energy, while the quantum mechanical harmonic oscillator must have the discrete energy levels given by Equation (3.78). Second, the potential energy of the mass will

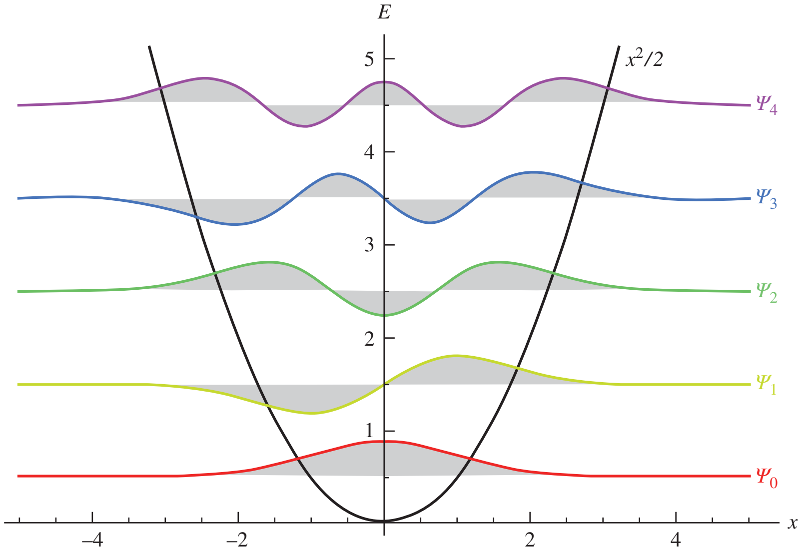


FIGURE 3.32
Solutions to the one-dimensional Schrödinger equation for the harmonic oscillator model. [Figure created by Oscar Castillo-Felisola using Sagemath. This figure is licensed under a Creative Commons Attribution-ShareAlike 3.0 Unported License.]

oscillate back and forth along the bottom of the parabola in Figure 3.32 in much the same way as the bob on the end of the pendulum will swing back and forth through its arc. Using classical mechanics, the oscillator will be moving faster in the center of its arc and therefore it will spend the least amount of time at the bottom of the potential energy well. The exact opposite is observed for the quantum mechanical harmonic oscillator—the probability density is greatest in the $v = 0$ (lowest energy) level at the exact center of the potential well. Third, while it is entirely possible for the classical oscillator to have zero energy (in fact this occurs every time the mass is restored to its equilibrium position), the quantum mechanical harmonic oscillator cannot be zero. This is due to the fact that if the potential energy were exactly zero, the position of the mass would be well defined to be at the center of the potential and the momentum would be well defined as exactly zero. This would violate the Heisenberg uncertainty principle. Fourth, it should be noted that the wave functions extend beyond the classical barrier for the potential energy (in other words, they leak outside of the parabola into the classically forbidden zone). In the limit of a very large v, as shown in Figure 3.33, the quantum harmonic oscillator spends more of

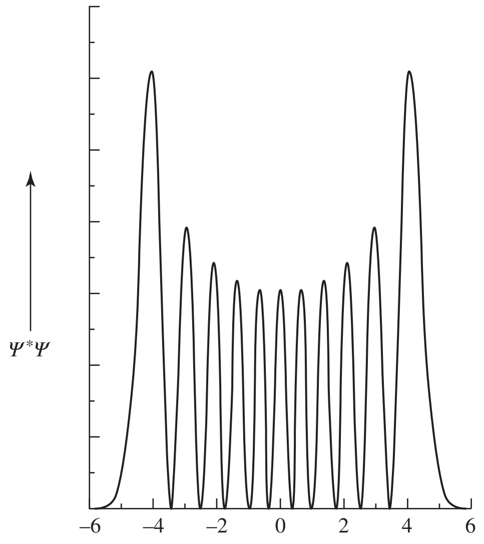


FIGURE 3.33
The probability function $\psi^*\psi$ for the harmonic oscillator with $v = 10$, showing how the potential energy for the quantum mechanical harmonic oscillator approaches that of the classical harmonic oscillator for very large values of v. [© Michael D Fayer, *Elements of Quantum Mechanics*, 2001, by permission of Oxford University Press, USA.]

its time near the edges of the parabola, in agreement with the classical observation that the oscillator has a higher probability at the extremes than in the center of the potential energy well. This correlation with classical mechanics at very large values of n was also observed in the particle in the box model and is known as the *correspondence principle*.

$$E_v = \hbar\omega\left(v + \frac{1}{2}\right), \quad \text{where } v = 0, 1, 2, \ldots \tag{3.78}$$

EXERCISES

3.1. Fluorescent light bulbs often consist of the line spectrum of Hg. Mercury has two strong atomic emission lines in the UV at 254 and 366 nm. (a) Calculate the frequency corresponding with each of these two wavelengths. (b) Calculate the energy of each line in units of joules.

3.2. Given that the (first) ionization energy of K is 419 kJ/mol, answer the following: (a) What is the maximum wavelength of light (in nm) necessary to ionize K metal? (b) Calculate the velocity of the ejected electron when a photon of UV light with $\lambda =$ 235 nm strikes the surface of K metal in an evacuated chamber.

3.3. Prove that $y = Ae^{2\pi i\upsilon \mathrm{tx}} + Be^{-2\pi i\upsilon \mathrm{tx}}$ is a solution to the one-dimensional wave equation given by Equation (3.3).

3.4. Indicate which of the following are eigenfunctions: (a) $\mathrm{d}^2/\mathrm{d}x^2$ (cos ax), (b) d/dt ($\mathrm{e}^{\mathrm{int}}$), (c) d/d$y$ ($y^2 - 2y$), (d) $\partial/\partial y$ (x^2 e^{6y}), (e) d/dx (sin ax). For each eigenfunction, determine the eigenvalue.

3.5. At what wavelength does the maximum in the cosmic background radiation from the Big Bang occur given that the average temperature of the universe is 2.725 K? In which region of the electromagnetic spectrum does this occur?

3.6. Given that the (first) ionization energy of Cs is 376 kJ/mol, answer the following: (a) What is the maximum wavelength of light (in nm) necessary to ionize Cs metal? (b) Calculate the velocity of the ejected electron when a photon of UV light with $\lambda = 235$ nm strikes the surface of Cs metal in an evacuated chamber.

3.7. The Paschen series of lines in the line spectrum of hydrogen occur in the near-IR. (a) Calculate the wavelength (in nm) of the series limit for the Paschen series of lines in the line spectrum of hydrogen. (b) The frequency of one line in the Paschen series of hydrogen is 2.34×10^{14} Hz. Using the Bohr model of the atom with its circular orbits, sketch this specific electronic transition.

3.8. Use the Rydberg equation to calculate the wavelengths of the first three lines in the Brackett series of the line spectrum of hydrogen.

3.9. Beams of neutrons are often used to obtain images of lightweight atoms in molecules. What velocity of neutrons is necessary to make a neutron beam having a wavelength of 0.0150 pm? (You will need to look up the rest mass of a neutron.)

3.10. Calculate the de Broglie wavelength for each of the following: (a) an electron with a kinetic energy of 120 eV, (b) a proton with a kinetic energy of 120 eV.

3.11. Calculate the velocity and kinetic energy of an electron in the first Bohr orbit ($a_0 = 52.9$ pm) of a hydrogen atom.

3.12. Using the Bohr model of the atom, answer the following questions: (a) Calculate the wavelength (nm) for the longest wavelength line of the Paschen series ($n_f = 3$). (b) Given that the energy of a line in the hydrogen spectrum is 1.94×10^{-18} J, draw a picture of the Bohr model of the atom showing this electronic transition.

3.13. Scientists have demonstrated the diffraction of matter for particles as large as a Buckyball (C_{60}). Given that the observed de Broglie wavelength for a beam of Buckyballs was 0.0025 nm, calculate the velocity that the Buckyballs were travelling.

3.14. One of the shortest LASER pulses ever generated was 100 as with an uncertainty of 12 as. Using the Heisenberg uncertainty principle, calculate the uncertainty in the frequency of the LASER pulse.

3.15. If it were possible to locate the position of an electron to within 10 pm, what would be the uncertainty in v?

3.16. Calculate the energy difference (in units of cm^{-1}) between the $n = 2$ energy level and the $n = 1$ energy level for the particle in a box model with length 1.0 nm.

3.17. To a first approximation, the six *pi* electrons in the molecule hexatriene, $CH_2{=}CH{-}CH{=}CH{-}CH{=}CH_2$, can be considered using the particle in a box model, where the length of the box is equal to the distance between the two end C atoms (or 867 pm). Calculate the energies for the first four energy levels using this model. Given that each energy level can hold two electrons in the ground state, the highest filled energy level will have $n = 3$ and the lowest unfilled energy level will have $n = 4$. Calculate the wavelength of an electronic transition between the $n = 3$ and the $n = 4$ energy levels.

3.18. The Bohr radius for the $n = 1$ level in hydrogen atom is 52.9 pm. Assuming that $a = 2r$ for the one-dimensional particle in a box model, calculate the energies for the first three quantum levels in units of megajoules per mole.

3.19. What is the degeneracy of the fifth lowest energy level for a particle in a box with lengths $a = b = 1.0$ nm and $c = 2.0$ nm?

3.20. Given that the force constant for a harmonic oscillator is 250 N/m, calculate the fundamental vibrational frequency and the zero-point energy for this vibrational mode.

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