40 QUANTUM MECHANICS

LEARNING GOALS

By studying this chapter, you will learn:

- About the wave function that describes the behavior of a particle and the Schrödinger equation that this function must satisfy.

- How to calculate the wave functions and energy levels for a particle confined to a box.

- How to analyze the quantum-mechanical behavior of a particle in a potential well.

- How quantum mechanics makes it possible for particles to go where Newtonian mechanics says they cannot.

- How to use quantum mechanics to analyze a harmonic oscillator.

? These containers hold solutions of microscopic semiconductor particles of different sizes. The particles glow when exposed to ultraviolet light; the smallest particles glow blue and the largest particles glow red. Why?

I n Chapter 39 we found that particles can behave like waves. In fact, it turns out that we can use the wave picture to completely describe the behavior of a particle. This approach, called *quantum mechanics,* is the key to understanding the behavior of matter on the molecular, atomic, and nuclear scales. In this chapter we'll see how to find the *wave function* of a particle by solving the *Schrödinger equation,* which is as fundamental to quantum mechanics as Newton's laws are to mechanics or as Maxwell's equations are to electromagnetism.

We'll begin with a quantum-mechanical analysis of a *free particle* that moves along a straight line without being acted on by forces of any kind. We'll then consider particles that are acted on by forces and are trapped in *bound states,* just as electrons are bound within an atom. We'll see that solving the Schrödinger equation automatically gives the possible energy levels for the system.

Besides energies, solving the Schrödinger equation gives us the probabilities of finding a particle in various regions. One surprising result is that there is a nonzero probability that microscopic particles will pass through thin barriers, even though such a process is forbidden by Newtonian mechanics.

In this chapter we'll consider the Schrödinger equation for one-dimensional motion only. In Chapter 41 we'll see how to extend this equation to three-dimensional problems such as the hydrogen atom. The hydrogen-atom wave functions will in turn form the foundation for our analysis of more complex atoms, of the periodic table of the elements, of x-ray energy levels, and of other properties of atoms.

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PhET: Fourier: Making Waves

40.1 Wave Functions and the One-Dimensional Schrödinger Equation

We have now seen compelling evidence that on an atomic or subatomic scale, an object such as an electron cannot be described simply as a classical, Newtonian point particle. Instead, we must take into account its *wave* characteristics. In the

Bohr model of the hydrogen atom (Section 39.3) we tried to have it both ways: We pictured the electron as a classical particle in a circular orbit around the nucleus, and used the de Broglie relation between particle momentum and wavelength to explain why only orbits of certain radii are allowed. As we saw in Section 39.6, however, the Heisenberg uncertainty principle tells us that a hybrid description of this kind can't be wholly correct. In this section we'll explore how to describe the state of a particle by using *only* the language of waves. This new description, called **quantum mechanics,** will replace the classical scheme of describing the state of a particle by its coordinates and velocity components.

Our new quantum-mechanical scheme for describing a particle has a lot in common with the language of classical wave motion. In Section 15.3 of Chapter 15, we described transverse waves on a string by specifying the position of each point in the string at each instant of time by means of a *wave function* $y(x, t)$ that represents the displacement from equilibrium, at time t, of a point on the string at a distance x from the origin (Fig. 40.1). Once we know the wave function for a particular wave motion, we know everything there is to know about the motion. For example, we can find the velocity and acceleration of any point on the string at any time. We worked out specific forms for these functions for *sinusoidal* waves, in which each particle undergoes simple harmonic motion.

We followed a similar pattern for sound waves in Chapter 16. The wave function $p(x, t)$ for a wave traveling along the x-direction represented the pressure variation at any point x and any time t. We used this language once more in Section 32.3, where we used *two* wave functions to describe the electric and magnetic fields in an electromagnetic wave.

Thus it's natural to use a wave function as the central element of our new language of quantum mechanics. The customary symbol for this wave function is the Greek letter psi, Ψ or ψ. In general, we'll use an uppercase Ψ to denote a function of all the space coordinates and time, and a lowercase ψ for a function of the space coordinates only—*not* of time. Just as the wave function $y(x, t)$ for mechanical waves on a string provides a complete description of the motion, so the wave function $\Psi(x, y, z, t)$ for a particle contains all the information that can be known about the particle.

40.1 These children are talking over a cup-and-string "telephone." The displacement of the string is completely described by a wave function $y(x, t)$. In an analogous way, a particle is completely described by a quantum-mechanical wave function $\Psi(x, y, z, t)$.

> **CAUTION** **Particle waves vs. mechanical waves** Unlike for mechanical waves on a string or sound waves in air, the wave function for a particle is *not* a mechanical wave that needs some material medium in order to propagate. The wave function describes the particle, but we cannot define the function itself in terms of anything material. We can only describe how it is related to physically observable effects. ▮

Waves in One Dimension

The wave function of a particle depends in general on all three dimensions of space. For simplicity, however, we'll begin our study of these functions by considering *one-dimensional* motion, in which a particle of mass m moves parallel to the x-axis and the wave function Ψ depends on the coordinate x and the time t only. (In the same way, we studied one-dimensional kinematics in Chapter 2 before going on to study two- and three-dimensional motion in Chapter 3.)

What does a one-dimensional quantum-mechanical wave look like, and what determines its properties? We can answer this question by first recalling the properties of a wave on a string. We saw in Section 15.3 that any wave function $y(x, t)$ that describes a wave on a string must satisfy the *wave equation:*

$$\frac{\partial^2 y(x, t)}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 y(x, t)}{\partial t^2} \qquad \text{(wave equation for waves on a string)} \qquad \text{(40.1)}$$

In Eq. (40.1) v is the speed of the wave, which is the same no matter what the wavelength. As an example, consider the following wave function for a

wave of wavelength λ and frequency f moving in the positive x-direction along a string:

$$y(x, t) = A\cos(kx - \omega t) + B\sin(kx - \omega t) \quad \text{(sinusoidal wave on a string)} \quad (40.2)$$

Here $k = 2\pi/\lambda$ is the *wave number* and $\omega = 2\pi f$ is the *angular frequency*. (We used these same quantities for mechanical waves in Chapter 15 and electromagnetic waves in Chapter 32.) The quantities A and B are constants that determine the amplitude and phase of the wave. The expression in Eq. (40.2) is a valid wave function if and only if it satisfies the wave equation, Eq. (40.1). To check this, take the first and second derivatives of $y(x, t)$ with respect to x and take the first and second derivatives with respect to t:

$$\frac{\partial y(x, t)}{\partial x} = -kA\sin(kx - \omega t) + kB\cos(kx - \omega t) \quad (40.3a)$$

$$\frac{\partial^2 y(x, t)}{\partial x^2} = -k^2 A\cos(kx - \omega t) - k^2 B\sin(kx - \omega t) \quad (40.3b)$$

$$\frac{\partial y(x, t)}{\partial t} = \omega A\sin(kx - \omega t) - \omega B\cos(kx - \omega t) \quad (40.3c)$$

$$\frac{\partial^2 y(x, t)}{\partial t^2} = -\omega^2 A\cos(kx - \omega t) - \omega^2 B\sin(kx - \omega t) \quad (40.3d)$$

If we substitute Eqs. (40.3b) and (40.3d) into the wave equation, Eq. (40.1), we get

$$-k^2 A\cos(kx - \omega t) - k^2 B\sin(kx - \omega t)$$

$$= \frac{1}{v^2}\left[-\omega^2 A\cos(kx - \omega t) - \omega^2 B\sin(kx - \omega t)\right] \quad (40.4)$$

For Eq. 40.4 to be satisfied at all coordinates x and all times t, the coefficients of the cosine function must be the same on both sides of the equation, and likewise for the coefficients of the sine function. You can see that both of these conditions will be satisfied if

$$k^2 = \frac{\omega^2}{v^2} \quad \text{or} \quad \omega = vk \quad \text{(waves on a string)} \quad (40.5)$$

From the definitions of angular frequency ω and wave number k, Eq. (40.5) is equivalent to

$$2\pi f = v\frac{2\pi}{\lambda} \quad \text{or} \quad v = \lambda f \quad \text{(waves on a string)}$$

This equation is just the familiar relationship among wave speed, wavelength, and frequency for waves on a string. So our calculation shows that Eq. (40.2) is a valid wave function for waves on a string for any values of A and B, provided that ω and k are related by Eq. (40.5).

What we need is a quantum-mechanical version of the wave equation, Eq. (40.1), valid for particle waves. We expect this equation to involve partial derivatives of the wave function $\Psi(x, t)$ with respect to x and with respect to t. However, this new equation *cannot* be the same as Eq. (40.1) for waves on a string because the relationship between ω and k is different. We can show this by considering a **free particle,** one that experiences no force at all as it moves along the x-axis. For such a particle the potential energy $U(x)$ has the same value for all x (recall from Chapter 7 that $F_x = -dU(x)/dx$, so zero force means the potential energy has zero derivative). For simplicity let $U = 0$ for all x. Then the energy of the free particle is equal to its kinetic energy, which we can express in terms of its momentum p:

$$E = \tfrac{1}{2}mv^2 = \frac{m^2 v^2}{2m} = \frac{(mv)^2}{2m} = \frac{p^2}{2m} \quad \text{(energy of a free particle)} \quad (40.6)$$

The de Broglie relations that we introduced in Section 39.1 tell us that the energy E is proportional to the angular frequency ω and the momentum p is proportional to the wave number:

$$E = hf = \frac{h}{2\pi}2\pi f = \hbar\omega \qquad (40.7a)$$

$$p = \frac{h}{\lambda} = \frac{h}{2\pi}\frac{2\pi}{\lambda} = \hbar k \qquad (40.7b)$$

Remember that $\hbar = h/2\pi$. If we substitute Eqs. (40.7) into Eq. (40.6), we find that the relationship between ω and k for a free particle is

$$\hbar\omega = \frac{\hbar^2 k^2}{2m} \qquad \text{(free particle)} \qquad (40.8)$$

Equation (40.8) is *very* different from the corresponding relationship for waves on a string, Eq. (40.5): The angular frequency ω for particle waves is proportional to the *square* of the wave number, while for waves on a string ω is directly proportional to k. Our task is therefore to construct a quantum-mechanical version of the wave equation whose free-particle solutions satisfy Eq. (40.8).

We'll attack this problem by assuming a sinusoidal wave function $\Psi(x, t)$ of the same form as Eq. (40.2) for a sinusoidal wave on a string. For a wave on a string, Eq. (40.2) represents a wave of wavelength $\lambda = 2\pi/k$ and frequency $f = \omega/2\pi$ propagating in the positive x-direction. By analogy, our sinsuoidal wave function $\Psi(x, t)$ represents a free particle of mass m, momentum $p = \hbar k$, and energy $E = \hbar\omega$ moving in the positive x-direction:

$$\Psi(x, t) = A\cos(kx - \omega t) + B\sin(kx - \omega t) \qquad \begin{array}{l}\text{(sinusoidal wave}\\ \text{function representing}\\ \text{a free particle)}\end{array} \qquad (40.9)$$

The wave number k and angular frequency ω in Eq. (40.9) must satisfy Eq. (40.8). If you look at Eq. (40.3b), you'll see that taking the second derivative of $\Psi(x, t)$ in Eq. (40.9) with respect to x gives us $\Psi(x, t)$ multiplied by $-k^2$. Hence if we multiply $\partial^2\Psi(x, t)/\partial x^2$ by $-\hbar^2/2m$, we get

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x, t)}{\partial x^2} = -\frac{\hbar^2}{2m}[-k^2 A\cos(kx - \omega t) - k^2 B\sin(kx - \omega t)]$$

$$= \frac{\hbar^2 k^2}{2m}[A\cos(kx - \omega t) + B\sin(kx - \omega t)] \qquad (40.10)$$

$$= \frac{\hbar^2 k^2}{2m}\Psi(x, t)$$

Equation (40.10) suggests that $(-\hbar^2/2m)\partial^2\Psi(x, t)/\partial x^2$ should be one side of our quantum-mechanical wave equation, with the other side equal to $\hbar\omega\Psi(x, t)$ in order to satisfy Eq. (40.8). If you look at Eq. (40.3c), you'll see that taking the *first* time derivative of $\Psi(x, t)$ in Eq. (40.9) brings out a factor of ω. So we'll make the educated guess that the right-hand side of our quantum-mechanical wave equation involves $\hbar = h/2\pi$ times $\partial\Psi(x, t)/\partial t$. So our tentative equation is

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x, t)}{\partial x^2} = C\hbar\frac{\partial\Psi(x, t)}{\partial t} \qquad (40.11)$$

At this point we include a constant C as a "fudge factor" to make sure that everything turns out right. Now let's substitute the wave function from Eq. (40.9) into Eq. (40.11). From Eq. (40.10) and Eq. (40.3c), we get

$$\frac{\hbar^2 k^2}{2m}\big[A\cos(kx - \omega t) + B\sin(kx - \omega t)\big]$$

$$= C\hbar\omega\big[A\sin(kx - \omega t) - B\cos(kx - \omega t)\big] \qquad (40.12)$$

From Eq. (40.8), $\hbar\omega = \hbar^2 k^2/2m$, so we can cancel these factors on the two sides of Eq. (40.12). What remains is

$$A\cos(kx - \omega t) + B\sin(kx - \omega t) = CA\sin(kx - \omega t)$$

$$- CB\cos(kx - \omega t) \qquad (40.13)$$

As in our discussion above of the wave equation for waves on a string, in order for Eq. (40.13) to be satisfied for all values of x and all values of t, the coefficients of the cosine function must be the same on both sides of the equation, and likewise for the coefficients of the sine function. Hence we have the following relationships among the coefficients A and B in Eq. (40.9) and the coefficient C in Eq. (40.11):

$$A = -CB \qquad (40.14a)$$

$$B = CA \qquad (40.14b)$$

If we use Eq. (40.14b) to eliminate B from Eq. (40.14a), we get $A = -C^2 A$, which means that $C^2 = -1$. Thus C is equal to the *imaginary* number $i = \sqrt{-1}$, and Eq. (40.11) becomes

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \Psi(x, t)}{\partial x^2} = i\hbar\frac{\partial \Psi(x, t)}{\partial t} \qquad \begin{array}{l}\text{(one-dimensional Schrödinger}\\ \text{equation for a free particle)}\end{array} \qquad (40.15)$$

Equation (40.15) is the one-dimensional **Schrödinger equation** for a free particle, developed in 1926 by the Austrian physicist Erwin Schrödinger (Fig. 40.2). The presence of the imaginary number i in Eq. (40.15) means that the solutions to the Schrödinger equation are complex quantities, with a real part and an imaginary part. (The imaginary part of $\Psi(x, t)$ is a real function multiplied by the imaginary number $i = \sqrt{-1}$.) An example is our free-particle wave function from Eq. (40.9). Since we found $C = i$ in Eqs. (40.14), it follows from Eq. (40.14b) that $B = iA$. Then Eq. (40.9) becomes

40.2 Erwin Schrödinger (1887–1961) developed the equation that bears his name in 1926, an accomplishment for which he shared (with the British physicist P. A. M. Dirac) the 1933 Nobel Prize in physics. His grave marker is adorned with a large letter ψ.

$$\Psi(x, t) = A\big[\cos(kx - \omega t) + i\sin(kx - \omega t)\big] \quad \begin{array}{l}\text{(sinusoidal wave}\\ \text{function representing}\\ \text{a free particle)}\end{array} \quad (40.16)$$

The real part of $\Psi(x, t)$ is $\text{Re}\,\Psi(x, t) = A\cos(kx - \omega t)$ and the imaginary part is $\text{Im}\,\Psi(x, t) = A\sin(kx - \omega t)$. Figure 40.3 graphs the real and imaginary parts of $\Psi(x, t)$ at $t = 0$, so $\Psi(x, 0) = A\cos kx + iA\sin kx$.

We can rewrite Eq. (40.16) using *Euler's formula*, which states that for any angle θ,

$$e^{i\theta} = \cos\theta + i\sin\theta$$

$$e^{-i\theta} = \cos(-\theta) + i\sin(-\theta) = \cos\theta - i\sin\theta \qquad (40.17)$$

Thus our sinusoidal free-particle wave function becomes

$$\Psi(x, t) = Ae^{i(kx - \omega t)} = Ae^{ikx}e^{-i\omega t} \qquad \begin{array}{l}\text{(sinusoidal wave function}\\ \text{representing a free particle)}\end{array} \qquad (40.18)$$

If k is positive in Eq. (40.16), the wave function represents a free particle moving in the positive x-direction with momentum $p = \hbar k$ and energy $E = \hbar\omega = \hbar^2 k^2/2m$. If k is negative, the momentum and hence the motion are in the negative x-direction. (With a negative value of k, the wavelength is $\lambda = 2\pi/|k|$).

Interpreting the Wave Function

The complex nature of the wave function for a free particle makes this function challenging to interpret. (We certainly haven't needed imaginary numbers before this point to describe real physical phenomena.) Here's how to think about this function: $\Psi(x, t)$ describes the *distribution* of a particle in space, just as the wave functions for an electromagnetic wave describe the distribution of the electric and magnetic fields. When we worked out interference and diffraction patterns in Chapters 35 and 36, we found that the intensity I of the radiation at any point in a pattern is proportional to the square of the electric-field magnitude—that is, to E^2. In the photon interpretation of interference and diffraction (see Section 38.4), the intensity at each point is proportional to the number of photons striking around that point or, alternatively, to the *probability* that any individual photon will strike around the point. Thus the square of the electric-field magnitude at each point is proportional to the probability of finding a photon around that point.

In exactly the same way, the square of the wave function of a particle at each point tells us about the probability of finding the particle around that point. More precisely, we should say the square of the *absolute value* of the wave function, $|\Psi|^2$. This is necessary because, as we have seen, the wave function is a complex quantity with real and imaginary parts.

For a particle that can move only along the x-direction, the quantity $|\Psi(x, t)|^2\,dx$ is the probability that the particle will be found at time t at a coordinate in the range from x to $x + dx$. The particle is most likely to be found in regions where $|\Psi|^2$ is large, and so on. This interpretation, first made by the German physicist Max Born (Fig. 40.4), requires that the wave function Ψ be *normalized*. That is, the integral of $|\Psi(x, t)|^2\,dx$ over all possible values of x must equal exactly 1. In other words, the probability is exactly 1, or 100%, that the particle is *somewhere*.

CAUTION **Interpreting $|\Psi|^2$** Note that $|\Psi(x, t)|^2$ itself is *not* a probability. Rather, $|\Psi(x, t)|^2\,dx$ is the probability of finding the particle between position x and position $x + dx$ at time t. If the length dx is made smaller, it becomes less likely that the particle will be found within that length, so the probability decreases. A better name for $|\Psi(x, t)|^2$ is the **probability distribution function,** since it describes how the probability of finding the particle at different locations is distributed over space. Another common name for $|\Psi(x, t)|^2$ is the *probability density.*

We can use the probability interpretation of $|\Psi|^2$ to get a better understanding of Eq. (40.18), the wave function for a free particle. This function decribes a particle that has a definite momentum $p = \hbar k$ in the x-direction and *no* uncertainty in momentum: $\Delta p_x = 0$. The Heisenberg uncertainty principle for position and momentum, Eq. (39.29), says that $\Delta x \Delta p_x \geq \hbar/2$. If Δp_x is zero, then Δx must be infinite, and we have no idea whatsoever where along the x-axis the particle can be found. (We saw a similar result for photons in Section 38.4.) We can show this by calculating the probability distribution function $|\Psi(x, t)|^2$. This is the product of Ψ and its *complex conjugate* Ψ^*. To find the complex conjugate of a complex number, we simply replace all i with $-i$. For example, the complex conjugate of $c = a + ib$, where a and b are real, is $c^* = a - ib$, so $|c|^2 = c^*c = (a + ib)(a - ib) = a^2 + b^2$ (recall that $i^2 = -1$). The complex conjugate of Eq. (40.18) is

$$\Psi^*(x, t) = A^* e^{-i(kx - \omega t)} = A^* e^{-ikx} e^{i\omega t}$$

(We have to allow for the possibility that the coefficient A is itself a complex number.) Hence the probability distribution function is

40.3 The spatial wave function $\Psi(x, t) = Ae^{i(kx - \omega t)}$ for a free particle of definite momentum $p = \hbar k$ is a complex function: It has both a real part and an imaginary part. These are graphed here as functions of x for $t = 0$.

Re $\Psi(x, 0) = A\cos kx$

Im $\Psi(x, 0) = A\sin kx$
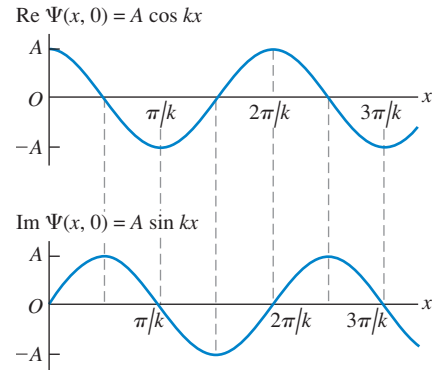
40.4 In 1926, the German physicist Max Born (1882–1970) devised the interpretation that $|\Psi|^2$ is the probability distribution function for a particle that is described by the wave function Ψ. He also coined the term "quantum mechanics" (in the original German, *Quantenmechanik*). For his contributions, Born shared (with Walther Bothe) the 1954 Nobel Prize in physics.

$$|\Psi(x,t)|^2 = \Psi^*(x,t)\Psi(x,t) = (A^* e^{-ikx} e^{i\omega t})(A e^{ikx} e^{-i\omega t})$$

$$= A^* A e^0 = |A|^2$$

The probability distribution function doesn't depend on position, which says that we are equally likely to find the particle *anywhere* along the x-axis! Mathematically, this is because the wave function $\Psi(x,t) = A e^{i(kx-\omega t)} = A[\cos(kx - \omega t) + i\sin(kx - \omega t)]$ is a sinusoidal function that extends all the way from $x = -\infty$ to $x = +\infty$ with the same amplitude A. This also means that the wave function can't be normalized: The integral of $|\Psi(x,t)|^2$ over all space would be infinite for any value of A.

Note also that the wave function in Eq. (40.18) describes a particle with a definite energy $E = \hbar\omega$, so there is zero uncertainty in energy: $\Delta E = 0$. The Heisenberg uncertainty principle for energy and time interval, $\Delta t\,\Delta E \geq \hbar$ [Eq. (39.30)], tells us that the time uncertainty Δt for this particle is infinite. In other words, we can have no idea *when* the particle will pass a given point on the x-axis. That also agrees with our result $|\Psi(x,t)|^2 = |A|^2$; the probability distribution function has the same value at all times.

Since we always have some idea of where a particle is, the wave function given in Eq. (40.18) isn't a realistic description. In our study of light in Section 38.4, we saw that we can make a wave function that's more *localized* in space by superimposing two or more sinusoidal functions. (This would be a good time to review that section.) As an illustration, let's calculate $|\Psi(x,t)|^2$ for a wave function of this kind.

Example 40.1   A localized free-particle wave function

The wave function $\Psi(x,t) = A e^{i(k_1 x - \omega_1 t)} + A e^{i(k_2 x - \omega_2 t)}$ is a superposition of *two* free-particle wave functions of the form given by Eq. (40.18). Both k_1 and k_2 are positive. (a) Show that this wave function satisfies the Schrödinger equation for a free particle of mass m. (b) Find the probability distribution function for $\Psi(x,t)$.

SOLUTION

IDENTIFY and SET UP: The wave functions $A e^{i(k_1 x - \omega_1 t)}$ and $A e^{i(k_2 x - \omega_2 t)}$ both represent particles moving in the positive x-direction, but with different momenta and kinetic energies: $p_1 = \hbar k_1$ and $E_1 = \hbar\omega_1 = \hbar^2 k_1^2/2m$ for the first function, $p_2 = \hbar k_2$ and $E_2 = \hbar\omega_2 = \hbar^2 k_2^2/2m$ for the second function. To test whether a superposition of these is also a valid wave function for a free particle, we'll see whether our function $\Psi(x,t)$ satisfies the free-particle Schrödinger equation, Eq. (40.15). It's useful to remember the derivatives of the exponential function: $(d/du)e^{au} = ae^{au}$ and $(d^2/du^2)e^{au} = a^2 e^{au}$. The probability distribution function $|\Psi(x,t)|^2$ is the product of $\Psi(x,t)$ and its complex conjugate.

EXECUTE: (a) If we substitute $\Psi(x,t)$ into Eq. (40.15), the left-hand side of the equation is

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \Psi(x,t)}{\partial x^2} = -\frac{\hbar^2}{2m}\frac{\partial^2(A e^{i(k_1 x - \omega_1 t)} + A e^{i(k_2 x - \omega_2 t)})}{\partial x^2}$$

$$= -\frac{\hbar^2}{2m}[(ik_1)^2 A e^{i(k_1 x - \omega_1 t)} + (ik_2)^2 A e^{i(k_2 x - \omega_2 t)}]$$

$$= \frac{\hbar^2 k_1^2}{2m} A e^{i(k_1 x - \omega_1 t)} + \frac{\hbar^2 k_2^2}{2m} A e^{i(k_2 x - \omega_2 t)}$$

The right-hand side is

$$i\hbar\frac{\partial \Psi(x,t)}{\partial t} = i\hbar\frac{\partial(A e^{i(k_1 x - \omega_1 t)} + A e^{i(k_2 x - \omega_2 t)})}{\partial t}$$

$$= i\hbar[(-i\omega_1)A e^{i(k_1 x - \omega_1 t)} + (-i\omega_2)A e^{i(k_2 x - \omega_2 t)}]$$

$$= \hbar\omega_1 A e^{i(k_1 x - \omega_1 t)} + \hbar\omega_2 A e^{i(k_2 x - \omega_2 t)}$$

The two sides *are* equal, provided that $\hbar\omega_1 = \hbar^2 k_1^2/2m$ and $\hbar\omega_2 = \hbar^2 k_2^2/2m$. These are just the relationships that we noted above. So we conclude that $\Psi(x,t) = A e^{i(k_1 x - \omega_1 t)} + A e^{i(k_2 x - \omega_2 t)}$ is a valid free-particle wave function. In general, if we take any two wave functions that are solutions of the Schrödinger equation and then make a superposition of these to create a third wave function $\Psi(x,t)$, then $\Psi(x,t)$ is also a solution of the Schrödinger equation.

(b) The complex conjugate of $\Psi(x,t)$ is

$$\Psi^*(x,t) = A^* e^{-i(k_1 x - \omega_1 t)} + A^* e^{-i(k_2 x - \omega_2 t)}$$

Hence

$$|\Psi(x,t)|^2$$

$$= \Psi^*(x,t)\Psi(x,t)$$

$$= (A^* e^{-i(k_1 x - \omega_1 t)} + A^* e^{-i(k_2 x - \omega_2 t)})(A e^{i(k_1 x - \omega_1 t)} + A e^{i(k_2 x - \omega_2 t)})$$

$$= A^* A \left[\begin{array}{l} e^{-i(k_1 x - \omega_1 t)}e^{i(k_1 x - \omega_1 t)} + e^{-i(k_2 x - \omega_2 t)}e^{i(k_2 x - \omega_2 t)} \\ + e^{-i(k_1 x - \omega_1 t)}e^{i(k_2 x - \omega_2 t)} + e^{-i(k_2 x - \omega_2 t)}e^{i(k_1 x - \omega_1 t)} \end{array} \right]$$

$$= |A|^2[e^0 + e^0 + e^{i[(k_2 - k_1)x - (\omega_2 - \omega_1)t]} + e^{-i[(k_2 - k_1)x - (\omega_2 - \omega_1)t]}]$$

To simplify this expression, recall that $e^0 = 1$. From Euler's formula, $e^{i\theta} = \cos\theta + i\sin\theta$ and $e^{-i\theta} = \cos\theta - i\sin\theta$, so $e^{i\theta} + e^{-i\theta} = 2\cos\theta$. Hence

$$|\Psi(x,t)|^2 = |A|^2\{2 + 2\cos[(k_2 - k_1)x - (\omega_2 - \omega_1)t]\}$$

$$= 2|A|^2\{1 + \cos[(k_2 - k_1)x - (\omega_2 - \omega_1)t]\}$$

EVALUATE: Figure 40.5 is a graph of the probability distribution function $|\Psi(x, t)|^2$ at $t = 0$. The value of $|\Psi(x, t)|^2$ varies between 0 and $4|A|^2$; probabilities can never be negative! The particle has become *somewhat* localized: The particle is most likely to be found near a point where $|\Psi(x, t)|^2$ is maximum (where the functions $Ae^{i(k_1x - \omega_1 t)}$ and $Ae^{i(k_2x - \omega_2 t)}$ interfere constructively) and is very unlikely to be found near a point where $|\Psi(x, t)|^2 = 0$ (where $Ae^{i(k_1x - \omega_1 t)}$ and $Ae^{i(k_2x - \omega_2 t)}$ interfere destructively). This is very similar to the phenomenon of beats for sound waves (see Section 16.7).
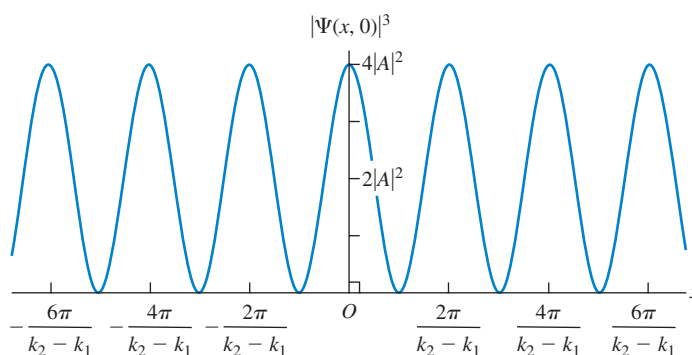
Note also that the probability distribution function is not stationary, but moves in the positive x-direction like the particle that it represents. To see this, recall from Section 15.3 that a sinusoidal wave given by $y(x, t) = A\cos(kx - \omega t)$ moves in the positive x-direction with velocity $v = \omega/k$; since $|\Psi(x, t)|^2$ includes a term $\cos[(k_2 - k_1)x - (\omega_2 - \omega_1)t]$, the probability distribution moves at a velocity $v_{av} = (\omega_2 - \omega_1)/(k_2 - k_1)$. The subscript "av" reminds us that v_{av} represents the *average* value of the particle's velocity.

The price we pay for localizing the particle somewhat is that, unlike a particle represented by Eq. (40.18), it no longer has either a definite momentum or a definite energy. That's consistent with the Heisenberg uncertainty principles: If we decrease the uncertainties about where a particle is and when it passes a certain point, the uncertainties in its momentum and energy must increase.

The average momentum of the particle is $p_{av} = (\hbar k_2 + \hbar k_1)/2$, the average of the momenta associated with the free-particle wave functions we added to create $\Psi(x, t)$. This corresponds to the particle having an average velocity $v_{av} = p_{av}/m = (\hbar k_2 + \hbar k_1)/2m$. Can you show that this is equal to the expression $v_{av} = (\omega_2 - \omega_1)/(k_2 - k_1)$ that we found above?

40.5 The probability distribution function at $t = 0$ for $\Psi(x, t) = Ae^{i(k_1x - \omega_1 t)} + Ae^{i(k_2x - \omega_2 t)}$.

Wave Packets

The wave function that we examined in Example 40.1 is not very well localized: The probability distribution function still extends from $x = -\infty$ to $x = +\infty$. Hence this wave function can't be normalized, either. To make a wave function that's more highly localized, imagine superposing two additional sinusoidal waves with different wave numbers and amplitudes so as to reinforce alternate maxima of $|\Psi(x, t)|^2$ in Fig. 40.5 and cancel out the in-between ones. Finally, if we superpose waves with a very large number of different wave numbers, we can construct a wave with only *one* maximum of $|\Psi(x, t)|^2$ (Fig. 40.6). Then, finally, we have something that begins to look like both a particle and a wave. It is a particle in the sense that it is localized in space; if we look from a distance, it may look like a point. But it also has a periodic structure that is characteristic of a wave.

A localized wave pulse like that shown in Fig. 40.6 is called a **wave packet.** We can represent a wave packet by an expression such as

$$\Psi(x, t) = \int_{-\infty}^{\infty} A(k)e^{i(kx - \omega t)}\, dk \qquad (40.19)$$

This integral represents a superposition of a very large number of waves, each with a different wave number k and angular frequency $\omega = \hbar k^2/2m$, and each with an amplitude $A(k)$ that depends on k.

There is an important relationship between the two functions $\Psi(x, t)$ and $A(k)$, which we show qualitatively in Fig. 40.7. If the function $A(k)$ is sharply peaked, as in Fig. 40.7a, we are superposing only a narrow range of wave numbers. The resulting wave pulse is then relatively broad (Fig. 40.7b). But if we use

40.6 Superposing a large number of sinusoidal waves with different wave numbers and appropriate amplitudes can produce a wave pulse that has a wavelength $\lambda_{av} = 2\pi/k_{av}$ and is localized within a region of space of length Δx. This localized pulse has aspects of both particle and wave.

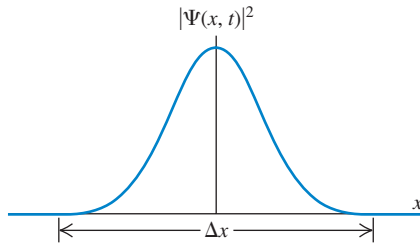(a) Real part of the wave function at time t

$$\text{Re}\Psi(x, t)$$
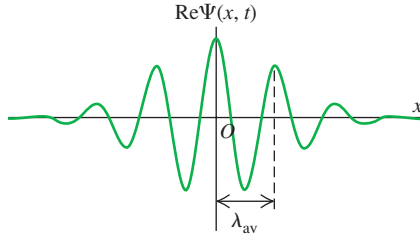
(b) Imaginary part of the wave function at time t

$$\text{Im }\Psi(x, t)$$
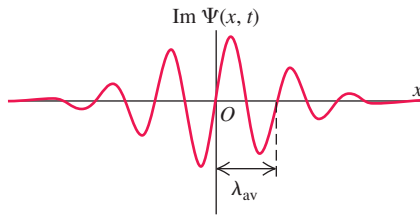
(c) Probability distribution function at time t

$$|\Psi(x, t)|^2$$

a wider range of wave numbers, so that the function $A(k)$ is broader (Fig. 40.7c), then the wave pulse is more narrowly localized (Fig. 40.7d). This is simply the uncertainty principle in action. A narrow range of k means a narrow range of $p_x = \hbar k$ and thus a small Δp_x; the result is a relatively large Δx. A broad range of k corresponds to a large Δp_x, and the resulting Δx is smaller. You can see that the uncertainty principle for position and momentum, $\Delta x \Delta p_x \geq \hbar/2$, is really just a consequence of the properties of integrals like Eq. (40.19).

CAUTION **Matter waves versus light waves in vacuum** We can regard both a wave packet that represents a particle and a short pulse of light from a laser as superpositions of waves of different wave numbers and angular frequencies. An important difference is that the speed of light in vacuum is the same for all wavelengths λ and hence all wave numbers $k = 2\pi/\lambda$, but the speed of a matter wave is *different* for different wavelengths. You can see this from the formula for the speed of the wave crests in a periodic wave, $v = \lambda f = \omega/k$. For a matter wave, $\omega = \hbar k^2/2m$, so $v = \hbar k/2m = h/2m\lambda$. Hence matter waves with longer wavelengths and smaller wave numbers travel more slowly than those with short wavelengths and large wave numbers. (This shouldn't be too surprising. The de Broglie relations that we learned in Section 39.1 tell us that shorter wavelength corresponds to greater momentum and hence a greater speed.) Since the individual sinusoidal waves that make up a wave packet travel at different speeds, the shape of the packet changes as it moves. That's why we've specified the time for which the wave packets in Figs. 40.6 and 40.7 are drawn; at later times, the packets become more spread out. By contrast, a pulse of light waves in vacuum retains the same shape at all times because all of its constituent sinusoidal waves travel together at the same speed. ▮

The One-Dimensional Schrödinger Equation with Potential Energy

The one-dimensional Schrödinger equation that we presented in Eq. (40.15) is valid only for free particles, for which the potential energy function is zero: $U(x) = 0$. But for an electron within an atom, a proton within an atomic nucleus, and many other real situations, the potential energy plays an important role. To study the behavior of matter waves in these situations, we need a version of the Schrödinger equation that describes a particle moving in the presence of a nonzero potential energy function $U(x)$. This equation is

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x, t)}{\partial x^2} + U(x)\Psi(x, t) = i\hbar\frac{\partial\Psi(x, t)}{\partial t} \qquad \text{(general one-dimensional Schrödinger equation)} \quad \text{(40.20)}$$

Note that if $U(x) = 0$, Eq. (40.20) reduces to the free-particle Schrödinger equation given in Eq. (40.15).

Here's the motivation behind Eq. (40.20). If $\Psi(x, t)$ is a sinusoidal wave function for a free particle, $\Psi(x, t) = Ae^{i(kx-\omega t)} = Ae^{ikx}e^{-i\omega t}$, the derivative terms in Eq. (40.20) become

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x, t)}{\partial x^2} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}(Ae^{ikx}e^{-i\omega t}) = -\frac{\hbar^2}{2m}(ik)^2(Ae^{ikx}e^{-i\omega t})$$

$$= \frac{\hbar^2 k^2}{2m}\Psi(x, t)$$

$$i\hbar\frac{\partial\Psi(x, t)}{\partial t} = i\hbar\frac{\partial}{\partial t}(Ae^{ikx}e^{-i\omega t}) = i\hbar(-i\omega)(Ae^{ikx}e^{-i\omega t}) = \hbar\omega\Psi(x, t)$$

In these expressions $(\hbar^2 k^2/2m)\Psi(x, t)$ is just the kinetic energy $K = p^2/2m = \hbar^2 k^2/2m$ multiplied by the wave function, and $\hbar\omega\Psi(x, t)$ is the total energy $E = \hbar\omega$ multiplied by the wave function. So for a wave function of this kind, Eq. (40.20) says that kinetic energy times $\Psi(x, t)$ plus potential energy times $\Psi(x, t)$ equals total energy times $\Psi(x, t)$. That's equivalent to the statement in

classical physics that the sum of kinetic energy and potential energy equals total mechanical energy: $K + U = E$.

The observations we've just made certainly aren't a *proof* that Eq. (40.20) is correct. The real reason we know this equation *is* correct is that it works: Predictions made with this equation agree with experimental results. In the remaining sections of this chapter we'll apply Eq. (40.20) to several physical situations, each with a different form of the function $U(x)$.

Stationary States

We saw in our discussion of wave packets that any free-particle wave function can be built up as a superposition of sinusoidal wave functions of the form $\Psi(x, t) = Ae^{ikx}e^{-i\omega t}$. Each such sinusoidal wave function corresponds to a state of definite energy $E = \hbar\omega = \hbar^2 k^2/2m$ and definite angular frequency $\omega = E/\hbar$, so we can rewrite these functions as $\Psi(x, t) = Ae^{ikx}e^{-iEt/\hbar}$. If the potential energy function $U(x)$ is nonzero, these sinusoidal wave functions do not satisfy the Schrödinger equation, Eq. (40.20), and so these functions cannot be the basic "building blocks" of more complicated wave functions. However, we can still write the wave function for a state of definite energy E in the form

$$\Psi(x, t) = \psi(x)e^{-iEt/\hbar} \qquad \begin{array}{l}\text{(time-dependent wave function} \\ \text{for a state of definite energy)}\end{array} \qquad \text{(40.21)}$$

That is, the wave function $\Psi(x, t)$ for a state of definite energy is the product of a *time-independent* wave function $\psi(x)$ and a factor $e^{-iEt/\hbar}$. (For the free-particle sinusoidal wave function, $\psi(x) = Ae^{ikx}$.) States of definite energy are of tremendous importance in quantum mechanics. For example, for each energy level in a hydrogen atom (Section 39.3) there is a specific wave function. It is possible for an atom to be in a state that does not have a definite energy. The wave function for any such state can be written as a combination of definite-energy wave functions, in precisely the same way that a free-particle wave packet can be written as a superposition of sinusoidal wave functions of definite energy as in Eq. (40.19).

A state of definite energy is commonly called a **stationary state.** To see where this name comes from, let's multiply Eq. (40.21) by its complex conjugate to find the probabilty distribution function $|\Psi|^2$:

$$\begin{aligned}|\Psi(x, t)|^2 &= \Psi^*(x, t)\Psi(x, t) = [\psi^*(x)e^{+iEt/\hbar}][\psi(x)e^{-iEt/\hbar}] \\ &= \psi^*(x)\psi(x)e^{(+iEt/\hbar)+(-iEt/\hbar)} = |\psi(x)|^2 e^0 \qquad \text{(40.22)} \\ &= |\psi(x)|^2\end{aligned}$$
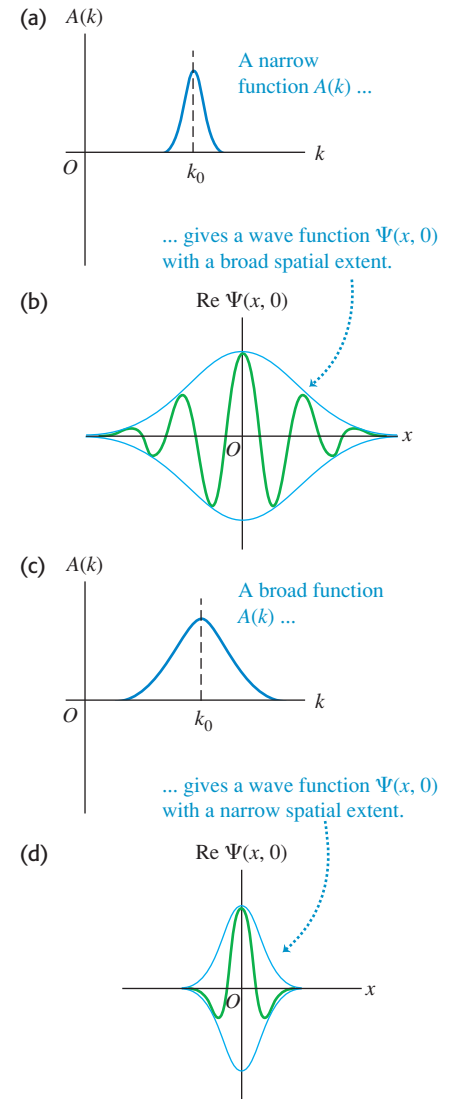
Since $|\psi(x)|^2$ does not depend on time, Eq. (40.22) shows that the same must be true for the probability distribution function $|\Psi(x, t)|^2$. This justifies the term "stationary state" for a state of definite energy.

> **CAUTION** **A stationary state does not mean a stationary particle** The name *stationary state* may lead you to think that the particle is not in motion if it is described by such a wave function. That's not the case. It's the *probability distribution* (that is, the relative likelihood of finding the particle at various positions), not the particle itself, that's stationary. ▮

The Schrödinger equation, Eq. (40.20), becomes quite a bit simpler for stationary states. To see this, we substitute Eq. (40.21) into Eq. (40.20):

$$-\frac{\hbar^2}{2m}\frac{\partial^2[\psi(x)e^{-iEt/\hbar}]}{\partial x^2} + U(x)\psi(x)e^{-iEt/\hbar} = i\hbar\frac{\partial[\psi(x)e^{-iEt/\hbar}]}{\partial t}$$

40.7 How varying the function $A(k)$ in the wave-packet expression, Eq. (40.19), changes the character of the wave function $\Psi(x, t)$ (shown here at a specific time $t = 0$).

(a) $A(k)$

A narrow function $A(k)$ ...

... gives a wave function $\Psi(x, 0)$ with a broad spatial extent.

(b)   Re $\Psi(x, 0)$

(c) $A(k)$

A broad function $A(k)$ ...

... gives a wave function $\Psi(x, 0)$ with a narrow spatial extent.

(d)   Re $\Psi(x, 0)$

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The derivative on the first term on the left-hand side is with respect to x, so the factor of $e^{-iEt/\hbar}$ comes outside of the derivative. Now we take the derivative with respect to t on the right-hand side of the equation:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}e^{-iEt/\hbar} + U(x)\psi(x)e^{-iEt/\hbar} = i\hbar\left(\frac{-iE}{\hbar}\right)[\psi(x)e^{-iEt/\hbar}]$$

$$= E\psi(x)e^{-iEt/\hbar}$$

If we divide both sides of this equation by $e^{-iEt/\hbar}$, we get

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + U(x)\psi(x) = E\psi(x) \qquad \text{(time-independent Schrödinger equation)} \qquad (40.23)$$

This is called the **time-independent Schrödinger equation.** The time-dependent factor $e^{-iEt/\hbar}$ does not appear, and Eq. (40.23) is an equation that involves only the time-independent wave function $\psi(x)$. We'll devote much of this chapter to solving this equation to find the definite-energy, stationary-state wave functions $\psi(x)$ and the corresponding values of E—that is, the energies of the allowed levels—for different physical situations.

Example 40.2   A stationary state

Consider the wave function $\psi(x) = A_1 e^{ikx} + A_2 e^{-ikx}$, where k is positive. Is this a valid time-independent wave function for a free particle in a stationary state? What is the energy corresponding to this wave function?

SOLUTION

IDENTIFY and SET UP: A valid stationary-state wave function for a free particle must satisfy the time-independent Schrödinger equation, Eq. (40.23), with $U(x) = 0$. To test the given function $\psi(x)$, we simply substitute it into the left-hand side of the equation. If the result is a constant times $\psi(x)$, then the wave function is indeed a solution and the constant is equal to the particle energy E.

EXECUTE: Substituting $\psi(x) = A_1 e^{ikx} + A_2 e^{-ikx}$ and $U(x) = 0$ into Eq. (40.23), we obtain

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = -\frac{\hbar^2}{2m}\frac{d^2(A_1 e^{ikx} + A_2 e^{-ikx})}{dx^2}$$

$$= -\frac{\hbar^2}{2m}[(ik)^2 A_1 e^{ikx} + (-ik)^2 A_2 e^{ikx}]$$

$$= \frac{\hbar^2 k^2}{2m}(A_1 e^{ikx} + A_2 e^{-ikx}) = \frac{\hbar^2 k^2}{2m}\psi(x)$$

The result is a constant times $\psi(x)$, so this $\psi(x)$ is indeed a valid stationary-state wave function for a free particle. Comparing with Eq. (40.23) shows that the constant on the right-hand side is the particle energy: $E = \hbar^2 k^2/2m$.

EVALUATE: Note that $\psi(x)$ is a *superposition* of two different wave functions: one function $(A_1 e^{ikx})$ that represents a particle with magnitude of momentum $p = \hbar k$ moving in the positive x-direction, and one function $(A_2 e^{-ikx})$ that represents a particle with the same magnitude of momentum moving in the negative x-direction. So while the combined wave function $\psi(x)$ represents a stationary state with a definite energy, this state does *not* have a definite momentum. We'll see in Section 40.2 that such a wave function can represent a *standing wave,* and we'll explore situations in which such standing matter waves can arise.

Test Your Understanding of Section 40.1   Does a wave packet given by Eq. (40.19) represent a stationary state? ∎

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ActivPhysics 20.2: Particle in a Box

40.2 Particle in a Box

An important problem in quantum mechanics is how to use the time-independent Schrödinger equation, Eq. (40.23), to determine the possible energy levels and the corresponding wave functions for various systems. The fundamental problem is then the following: For a given potential energy function $U(x)$, what are the possible stationary-state wave functions $\psi(x)$, and what are the corresponding energies E?

In Section 40.1 we solved this problem for the case $U(x) = 0$, corresponding to a *free* particle. The allowed wave functions and corresponding energies are

$$\psi(x) = Ae^{ikx} \quad E = \frac{\hbar^2 k^2}{2m} \quad \text{(free particle)} \quad (40.24)$$

The wave number k is equal to $2\pi/\lambda$, where λ is the wavelength. We found that k can have any real value, so the energy E of a free particle can have any value from zero to infinity. Furthermore, the particle can be found with equal probability at any value of x from $-\infty$ to $+\infty$.

Now let's look at a simple model in which a particle is *bound* so that it cannot escape to infinity, but rather is confined to a restricted region of space. Our system consists of a particle confined between two rigid walls separated by a distance L (Fig. 40.8). The motion is purely one dimensional, with the particle moving along the x-axis only and the walls at $x = 0$ and $x = L$. The potential energy corresponding to the rigid walls is infinite, so the particle cannot escape; between the walls, the potential energy is zero (Fig. 40.9). This situation is often described as a **"particle in a box."** This model might represent an electron that is free to move within a long, straight molecule or along a very thin wire.

Wave Functions for a Particle in a Box

To solve the Schrödinger equation for this system, we begin with some restrictions on the particle's stationary-state wave function $\psi(x)$. Because the particle is confined to the region $0 \leq x \leq L$, we expect the probability distribution function $|\Psi(x, t)|^2 = |\psi(x)|^2$ and the wave function $\psi(x)$ to be zero outside that region. This agrees with the Schrödinger equation: If the term $U(x)\psi(x)$ in Eq. (40.23) is to be finite, then $\psi(x)$ must be zero where $U(x)$ is infinite.

Furthermore, $\psi(x)$ must be a *continuous* function to be a mathematically well-behaved solution to the Schrödinger equation. This implies that $\psi(x)$ must be zero at the region's boundary, $x = 0$ and $x = L$. These two conditions serve as *boundary conditions* for the problem. They should look familiar, because they are the same conditions that we used to find the normal modes of a vibrating string in Section 15.8 (Fig. 40.10); you should review that discussion.

An additional condition is that to calculate the second derivative $d^2\psi(x)/dx^2$ in Eq. (40.23), the *first* derivative $d\psi(x)/dx$ must also be continuous except at points where the potential energy becomes infinite (as it does at the walls of the box). This is analogous to the requirement that a vibrating string, like those shown in Fig. 40.10, can't have any kinks in it (which would correspond to a discontinuity in the first derivative of the wave function) except at the ends of the string.

We now solve for the wave functions in the region $0 \leq x \leq L$ subject to the above conditions. In this region $U(x) = 0$, so the wave function in this region must satisfy

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} = E\psi(x) \quad \text{(particle in a box)} \quad (40.25)$$

Equation (40.25) is the *same* Schrödinger equation as for a free particle, so it is tempting to conclude that the wave functions and energies are given by Eq. (40.24). It is true that $\psi(x) = Ae^{ikx}$ satisfies the Schrödinger equation with $U(x) = 0$, is continuous, and has a continuous first derivative $d\psi(x)/dx = ikAe^{ikx}$. However, this wave function does *not* satisfy the boundary conditions that $\psi(x)$ must be zero at $x = 0$ and $x = L$: At $x = 0$ the wave function in Eq. (40.24) is equal to $Ae^0 = A$, and at $x = L$ it is equal to Ae^{ikL}. (These would be equal to zero if $A = 0$, but then the wave function would be zero and there would be no particle at all!)

The way out of this dilemma is to recall Example 40.2 (Section 40.1), in which we found that a more general stationary-state solution to the time-independent Schrödinger equation with $U(x) = 0$ is

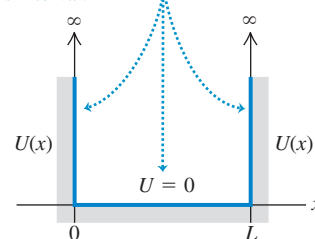$$\psi(x) = A_1 e^{ikx} + A_2 e^{-ikx} \quad (40.26)$$

40.8 The Newtonian view of a particle in a box.

A particle with mass m moves along a straight line at constant speed, bouncing between two rigid walls a distance L apart.
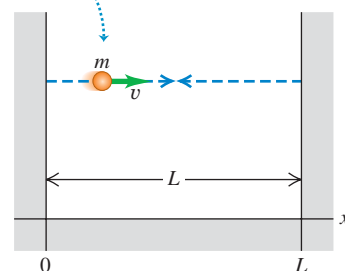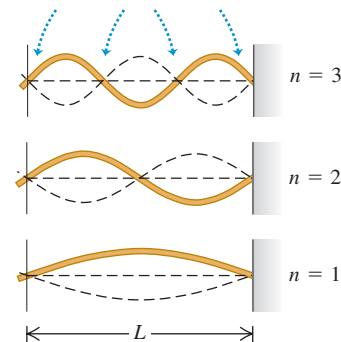

40.9 The potential-energy function for a particle in a box.

The potential energy U is zero in the interval $0 < x < L$ and is infinite everywhere outside this interval.

40.10 Normal modes of vibration for a string with length L, held at both ends.

Each end is a node, and there are $n - 1$ additional nodes between the ends.

The length is an integral number of half-wavelengths: $L = n\lambda_n/2$.

This wave function is a superposition of two waves: one traveling in the $+x$-direction of amplitude A_1, and one traveling in the $-x$-direction with the same wave number but amplitude A_2. This is analogous to a standing wave on a string (Fig. 40.10), which we can regard as the superposition of two sinusoidal waves propagating in opposite directions (see Section 15.7). The energy that corresponds to Eq. (40.26) is $E = \hbar^2 k^2/2m$, just as for a single wave.

To see whether the wave function given by Eq. (40.26) can satisfy the boundary conditions, let's first rewrite it in terms of sines and cosines using Euler's formula, Eq. (40.17):

$$\psi(x) = A_1(\cos kx + i \sin kx) + A_2[\cos(-kx) + i \sin(-kx)]$$

$$= A_1(\cos kx + i \sin kx) + A_2(\cos kx - i \sin kx) \qquad (40.27)$$

$$= (A_1 + A_2)\cos kx + i(A_1 - A_2)\sin kx$$

At $x = 0$ this is equal to $\psi(0) = A_1 + A_2$, which must equal zero if we are to satisfy the boundary condition at that point. Hence $A_2 = -A_1$, and Eq. (40.27) becomes

$$\psi(x) = 2iA_1 \sin kx = C \sin kx \qquad (40.28)$$

We have simplified the expression by introducing the constant $C = 2iA_1$. (We'll come back to this constant later.) We can also satisfy the second boundary condition that $\psi = 0$ at $x = L$ by choosing values of k such that $kL = n\pi$ ($n = 1, 2, 3, \dots$). Hence Eq. (40.28) does indeed give the stationary-state wave functions for a particle in a box in the region $0 \le x \le L$. (Outside this region, $\psi(x) = 0$.) The possible values of k and the wavelength $\lambda = 2\pi/k$ are

$$k = \frac{n\pi}{L} \quad \text{and} \quad \lambda = \frac{2\pi}{k} = \frac{2L}{n} \quad (n = 1, 2, 3, \dots) \qquad (40.29)$$

Just as for the string in Fig. 40.10, the length L of the region is an integral number of half-wavelengths.

Energy Levels for a Particle in a Box

The possible energy levels for a particle in a box are given by $E = \hbar^2 k^2/2m = p^2/2m$, where $p = \hbar k = (h/2\pi)(2\pi/\lambda) = h/\lambda$ is the magnitude of momentum of a free particle with wave number k and wavelength λ. This makes sense, since inside the region $0 \le x \le L$ the potential energy is zero and the energy is all kinetic. For each value of n, there are corresponding values of p, λ, and E; let's call them p_n, λ_n, and E_n. Putting the pieces together, we get

$$p_n = \frac{h}{\lambda_n} = \frac{nh}{2L} \qquad (40.30)$$

and so the energy levels for a particle in a box are

$$E_n = \frac{p_n{}^2}{2m} = \frac{n^2 h^2}{8mL^2} = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \quad (n = 1, 2, 3, \dots) \qquad \begin{array}{l}\text{(energy levels,}\\ \text{particle in a box)}\end{array} \quad (40.31)$$

Each energy level has its own value of the quantum number n and a corresponding wave function, which we denote by ψ_n. When we replace k in Eq. (40.28) by $n\pi/L$ from Eq. (40.29), we find

$$\psi_n(x) = C \sin\frac{n\pi x}{L} \quad (n = 1, 2, 3, \dots) \qquad (40.32)$$

The energy-level diagram in Fig. 40.11a shows the five lowest levels for a particle in a box. The energy levels are proportional to n^2, so successively higher levels are spaced farther and farther apart. There are an infinite number of levels because the walls are perfectly rigid; even a particle of infinitely great kinetic
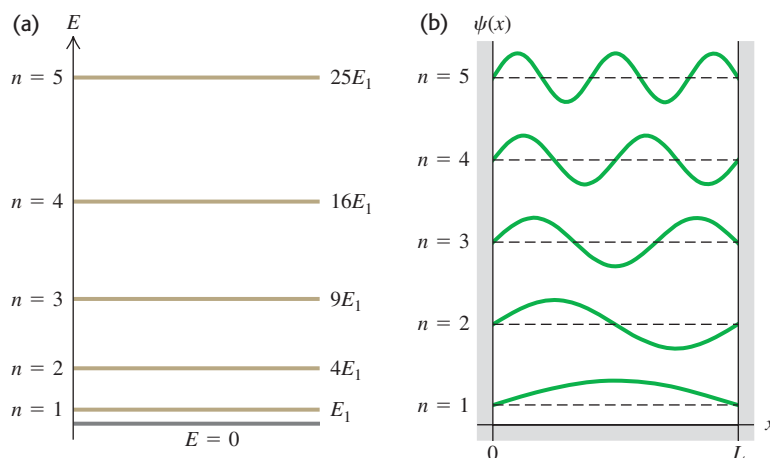
40.11 (a) Energy-level diagram for a particle in a box. Each energy is n^2E_1, where E_1 is the ground-level energy. (b) Wave functions for a particle in a box, with $n = 1, 2, 3, 4,$ and 5. **CAUTION:** The five graphs have been displaced vertically for clarity, as in Fig. 40.10. Each of the horizontal dashed lines represents $\psi = 0$ for the respective wave function.

energy is confined within the box. Figure 40.11b shows graphs of the wave functions $\psi_n(x)$ for $n = 1, 2, 3, 4,$ and 5. Note that these functions look identical to those for a standing wave on a string (see Fig. 40.10).

> **CAUTION** **A particle in a box cannot have zero energy** Note that the energy of a particle in a box *cannot* be zero. Equation (40.31) shows that $E = 0$ would require $n = 0$, but substituting $n = 0$ into Eq. (40.32) gives a zero wave function. Since a particle is described by a *nonzero* wave function, this means that there cannot be a particle with $E = 0$. This is a consequence of the Heisenberg uncertainty principle: A particle in a zero-energy state would have a definite value of momentum (precisely zero), so its position uncertainty would be infinite and the particle could be found anywhere along the x-axis. But this is impossible, since a particle in a box can be found only between $x = 0$ and $x = L$. Hence $E = 0$ is not allowed. By contrast, the allowed stationary-state wave functions with $n = 1, 2, 3, \ldots$ do not represent states of definite momentum (each is an equal mixture of a state of x-momentum $+p_n = nh/2L$ and a state of x-momentum $-p_n = -nh/2L$). Hence each stationary state has a nonzero momentum uncertainty, consistent with having a finite position uncertainty. ▮

Example 40.3   **Electron in an atom-size box**

Find the first two energy levels for an electron confined to a one-dimensional box 5.0×10^{-10} m across (about the diameter of an atom).

SOLUTION

IDENTIFY and SET UP: This problem uses what we have learned in this section about a particle in a box. The first two energy levels correspond to $n = 1$ and $n = 2$ in Eq. (40.31).

EXECUTE: From Eq. (40.31),

$$E_1 = \frac{h^2}{8mL^2} = \frac{(6.626 \times 10^{-34}\ \text{J} \cdot \text{s})^2}{8(9.109 \times 10^{-31}\ \text{kg})(5.0 \times 10^{-10}\ \text{m})^2}$$

$$= 2.4 \times 10^{-19}\ \text{J} = 1.5\ \text{eV}$$

$$E_2 = \frac{2^2 h^2}{8mL^2} = 4E_1 = 9.6 \times 10^{-19}\ \text{J} = 6.0\ \text{eV}$$

EVALUATE: The difference between the first two energy levels is $E_2 - E_1 = 4.5$ eV. An electron confined to a box is different from an electron bound in an atom, but it is reassuring that this result is of the same order of magnitude as the difference between actual atomic energy levels.

You can also show that for a proton or neutron ($m = 1.67 \times 10^{-27}$ kg) confined to a box 1.1×10^{-14} m across (the width of a medium-sized atomic nucleus), the energies of the first two levels are about a million times larger: $E_1 = 1.7 \times 10^6$ eV $= 1.7$ MeV, $E_2 = 4E_1 = 6.8$ MeV, $E_2 - E_1 = 5.1$ MeV. This suggests why nuclear reactions (which involve transitions between energy levels in nuclei) release so much more energy than chemical reactions (which involve transitions between energy levels of electrons in atoms).

Finally, you can show (see Exercise 40.11) that the energy levels of a billiard ball ($m = 0.2$ kg) confined to a box 1.3 m across—the width of a billard table—are separated by about 5×10^{-67} J. Quantum effects won't disturb a game of billiards.

Probability and Normalization

Let's look a bit more closely at the wave functions for a particle in a box, keeping in mind the *probability* interpretation of the wave function ψ that we discussed in Section 40.1. In our one-dimensional situation the quantity $|\psi(x)|^2\ dx$ is proportional

40.12 Graphs of (a) $\psi(x)$ and (b) $|\psi(x)|^2$ for the first three wave functions ($n = 1, 2, 3$) for a particle in a box. The horizontal dashed lines represent $\psi(x) = 0$ and $|\psi(x)|^2 = 0$ for each of the three levels. The value of $|\psi(x)|^2 dx$ at each point is the probability of finding the particle in a small interval dx about the point. As in Fig. 40.11b, the three graphs in each part have been displaced vertically for clarity.

(a) $\psi(x)$

(b) $|\psi(x)|^2$
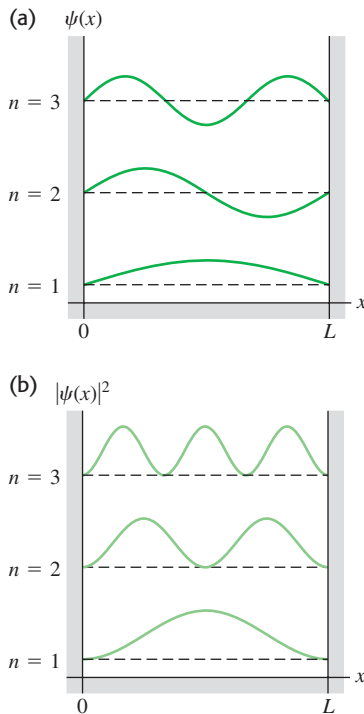
to the probability that the particle will be found within a small interval dx about x. For a particle in a box,

$$|\psi(x)|^2 dx = C^2 \sin^2 \frac{n\pi x}{L} dx$$

Figure 40.12 shows graphs of both $\psi(x)$ and $|\psi(x)|^2$ for $n = 1, 2$, and 3. Note that not all positions are equally likely. By contrast, in classical mechanics the particle is equally likely to be found at any position between $x = 0$ and $x = L$. We see from Fig. 40.12b that $|\psi(x)|^2 = 0$ at some points, so there is zero probability of finding the particle at exactly these points. Don't let that bother you; the uncertainty principle has already shown us that we can't measure position exactly. The particle is localized only to be somewhere between $x = 0$ and $x = L$.

The particle must be *somewhere* on the x-axis—that is, somewhere between $x = -\infty$ and $x = +\infty$. So the *sum* of the probabilities for all the dx's everywhere (the *total* probability of finding the particle) must equal 1. That's the normalization condition that we discussed in Section 40.1:

$$\int_{-\infty}^{\infty} |\psi(x)|^2 \, dx = 1 \qquad \text{(normalization condition)} \qquad (40.33)$$

A wave function is said to be *normalized* if it has a constant such as C in Eq. (40.32) that is calculated to make the total probability equal 1 in Eq. (40.33). For a normalized wave function, $|\psi(x)|^2 dx$ is not merely proportional to, but *equals,* the probability of finding the particle between the coordinates x and $x + dx$. That's why we call $|\psi(x)|^2$ the probability distribution function. (In Section 40.1 we called $|\Psi(x, t)|^2$ the probability distribution function. For the case of a stationary-state wave function, however, $|\Psi(x, t)|^2$ is equal to $|\psi(x)|^2$.)

Let's normalize the particle-in-a-box wave functions $\psi_n(x)$ given by Eq. (40.32). Since $\psi_n(x)$ is zero except between $x = 0$ and $x = L$, Eq. (40.33) becomes

$$\int_0^L C^2 \sin^2 \frac{n\pi x}{L} dx = 1 \qquad (40.34)$$

You can evaluate this integral using the trigonometric identity $\sin^2 \theta = \frac{1}{2}(1 - \cos 2\theta)$; the result is $C^2 L/2$. Thus our probability interpretation of the wave function demands that $C^2 L/2 = 1$, or $C = (2/L)^{1/2}$; the constant C is *not* arbitrary. (This is in contrast to the classical vibrating string problem, in which C represents an amplitude that depends on initial conditions.) Thus the normalized stationary-state wave functions for a particle in a box are

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \quad (n = 1, 2, 3, \dots) \quad \text{(particle in a box)} \qquad (40.35)$$

Example 40.4   **A nonsinusoidal wave function?**

(a) Show that $\psi(x) = Ax + B$, where A and B are constants, is a solution of the Schrödinger equation for an $E = 0$ energy level of a particle in a box. (b) What constraints do the boundary conditions at $x = 0$ and $x = L$ place on the constants A and B?

SOLUTION

IDENTIFY and SET UP: To be physically reasonable, a wave function must satisfy both the Schrödinger equation and the appropriate boundary conditions. In part (a) we'll substitute $\psi(x)$ into the

Schrödinger equation for a particle in a box, Eq. (40.25), to determine whether it is a solution. In part (b) we'll see what restrictions on $\psi(x)$ arise from applying the boundary conditions that $\psi(x) = 0$ at $x = 0$ and $x = L$.

EXECUTE: (a) From Eq. (40.25), the Schrödinger equation for an $E = 0$ energy level of a particle in a box is

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} = E\psi(x) = 0$$

in the region $0 \leq x \leq L$. Differentiating $\psi(x) = Ax + B$ twice with respect to x gives $d^2\psi(x)/dx^2 = 0$, so the left side of the equation is zero, and so $\psi(x) = Ax + B$ is a solution of this Schrödinger equation for $E = 0$. (Note that both $\psi(x)$ and its derivative $d\psi(x)/dx = A$ are continuous functions, as they must be.)

(b) Applying the boundary condition at $x = 0$ gives $\psi(0) = B = 0$, and so $\psi(x) = Ax$. Applying the boundary condition at $x = L$ gives $\psi(L) = AL = 0$, so $A = 0$. Hence $\psi(x) = 0$ both

inside the box ($0 \leq x \leq L$) *and outside:* There is *zero* probability of finding the particle anywhere with this wave function, and so $\psi(x) = Ax + B$ is *not* a physically valid wave function.

EVALUATE: The moral is that there are many functions that satisfy the Schrödinger equation for a given physical situation, but most of these—including the function considered here—have to be rejected because they don't satisfy the appropriate boundary conditions.

Time Dependence

Finally, we note that the wave functions $\psi_n(x)$ in Eq. (40.35) depend only on the *spatial* coordinate x. Equation (40.21) shows that if $\psi(x)$ is the wave function for a state of definite energy E, the full time-dependent wave function is $\Psi(x, t) = \psi(x)e^{-iEt/\hbar}$. Hence the *time-dependent* stationary-state wave functions for a particle in a box are

$$\Psi_n(x, t) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) e^{-iE_n t/\hbar} \qquad (n = 1, 2, 3, \dots) \qquad (40.36)$$

In this expression the energies E_n are given by Eq. (40.31). The higher the quantum number n, the greater the angular frequency $\omega_n = E_n/\hbar$ at which the wave function oscillates. Note that since $\left|e^{-iE_n t/\hbar}\right|^2 = e^{+iE_n t/\hbar}e^{-iE_n t/\hbar} = e^0 = 1$, the probability distribution function $\left|\Psi_n(x, t)\right|^2 = (2/L)\sin^2(n\pi x/L)$ is independent of time and does *not* oscillate. (Remember, this is why we say that these states of definite energy are *stationary*.)

Test Your Understanding of Section 40.2 If a particle in a box is in the nth energy level, what is the average value of its x-component of momentum p_x? (i) $nh/2L$; (ii) $(\sqrt{2}/2)nh/L$; (iii) $(1/\sqrt{2})nh/L$; (iv) $[1/(2\sqrt{2})]nh/L$; (v) zero.

MP

40.3 **Potential Wells**

MasteringPHYSICS

**PhET:** Double Wells and Covalent Bonds
PhET: Quantum Bound States
ActivPhysics 20.1: Potential Energy Diagrams
ActivPhysics 20.3: Potential Wells

A **potential well** is a potential-energy function $U(x)$ that has a minimum. We introduced this term in Section 7.5, and we also used it in our discussion of periodic motion in Chapter 14. In Newtonian mechanics a particle trapped in a potential well can vibrate back and forth with periodic motion. Our first application of the Schrödinger equation, the particle in a box, involved a rudimentary potential well with a function $U(x)$ that is zero within a certain interval and infinite everywhere else. As we mentioned in Section 40.2, this function corresponds to a few situations found in nature, but the correspondence is only approximate.

A better approximation to several actual physical situations is a **finite well,** which is a potential well with straight sides but *finite* height. Figure 40.13 shows a potential-energy function that is zero in the interval $0 \leq x \leq L$ and has the value U_0 outside this interval. This function is often called a **square-well potential.** It could serve as a simple model of an electron within a metallic sheet with thickness L, moving perpendicular to the surfaces of the sheet. The electron can move freely inside the metal but has to climb a potential-energy barrier with height U_0 to escape from either surface of the metal. The energy U_0 is related to the *work function* that we discussed in Section 38.1 in connection with the photoelectric effect. In three dimensions, a spherical version of a finite well gives an approximate description of the motions of protons and neutrons within a nucleus.

40.13 A square-well potential.

The potential energy U is zero within the potential well (in the interval $0 \leq x \leq L$) and has the constant value U_0 outside this interval.

Bound States of a Square-Well Potential

In Newtonian mechanics, the particle is trapped (localized) in a well if the total mechanical energy E is less than U_0. In quantum mechanics, such a trapped state is often called a **bound state.** All states are bound for an infinitely deep well like
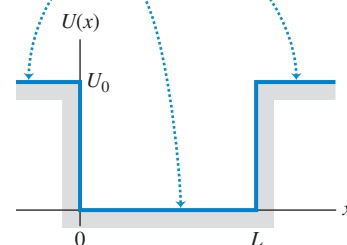
the one we described in Section 40.2. For a finite well like that shown in Fig. 40.13, if E is greater than U_0, the particle is *not* bound.

Let's see how to solve the Schrödinger equation for the bound states of a square-well potential. Our goal is to find the energies and wave functions for which $E < U_0$. The easiest approach is to consider separately the regions where $U = 0$ and where $U = U_0$. Where $U = 0$, the time-independent Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x) \quad \text{or} \quad \frac{d^2\psi(x)}{dx^2} = -\frac{2mE}{\hbar^2}\psi(x) \qquad (40.37)$$

This is the same as Eq. (40.25) from Section 40.2, which describes a particle in a box. As in Section 40.2, we can express the solutions of this equation as combinations of $\cos kx$ and $\sin kx$, where $E = \hbar^2 k^2/2m$. We can rewrite the relationship between E and k as $k = \sqrt{2mE}/\hbar$. Hence inside the square well $(0 \le x \le L)$ we have

$$\psi(x) = A\cos\left(\frac{\sqrt{2mE}}{\hbar}x\right) + B\sin\left(\frac{\sqrt{2mE}}{\hbar}x\right) \quad \text{(inside the well)} \qquad (40.38)$$

where A and B are constants. So far, this looks a lot like the particle-in-a-box analysis in Section 40.2. The difference is that for the square-well potential, the potential energy outside the well is not infinite, so the wave function $\psi(x)$ outside the well is *not* zero.

For the regions outside the well $(x < 0$ and $x > L)$ the potential-energy function in the time-independent Schrodinger equation is $U = U_0$:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + U_0\psi(x) = E\psi(x) \quad \text{or} \quad \frac{d^2\psi(x)}{dx^2} = \frac{2m(U_0 - E)}{\hbar^2}\psi(x) \quad (40.39)$$

The quantity $U_0 - E$ is positive, so the solutions of this equation are exponential. Using κ (the Greek letter kappa) to represent the quantity $[2m(U_0 - E)]^{1/2}/\hbar$ and taking κ as positive, we can write the solutions as

$$\psi(x) = Ce^{\kappa x} + De^{-\kappa x} \qquad \text{(outside the well)} \qquad (40.40)$$

where C and D are constants with different values in the two regions $x < 0$ and $x > L$. Note that ψ can't be allowed to approach infinity as $x \to +\infty$ or $x \to -\infty$. [If it did, we wouldn't be able to satisfy the normalization condition, Eq. (40.33).] This means that in Eq. (40.40), we must have $D = 0$ for $x < 0$ and $C = 0$ for $x > L$.

Our calculations so far show that the bound-state wave functions for a finite well are sinusoidal inside the well [Eq. (40.38)] and exponential outside it [Eq. (40.40)]. We have to *match* the wave functions inside and outside the well so that they satisfy the boundary conditions that we mentioned in Section 40.2: $\psi(x)$ and $d\psi(x)/dx$ must be continuous at the boundary points $x = 0$ and $x = L$. If the wave function $\psi(x)$ or the slope $d\psi(x)/dx$ were to change discontinuously at a point, the second derivative $d^2\psi(x)/dx^2$ would be *infinite* at that point. That would violate the time-independent Schrödinger equation, Eq. (40.23), which says that at every point $d^2\psi(x)/dx^2$ is proportional to $U - E$. For a finite well $U - E$ is finite everywhere, so $d^2\psi(x)/dx^2$ must also be finite everywhere.

Matching the sinusoidal and exponential functions at the boundary points so that they join smoothly is possible only for certain specific values of the total energy E, so this requirement determines the possible energy levels of the finite square well. There is no simple formula for the energy levels as there was for the infinitely deep well. Finding the levels is a fairly complex mathematical problem that requires solving a transcendental equation by numerical approximation; we won't go into the details. Figure 40.14 shows the general shape of a possible wave function. The most striking features of this wave function are the

40.14 A possible wave function for a particle in a finite potential well. The function is sinusoidal inside the well $(0 \le x \le L)$ and exponential outside it. It approaches zero asymptotically at large $|x|$. The functions must join smoothly at $x = 0$ and $x = L$; the wave function and its derivative must be continuous.
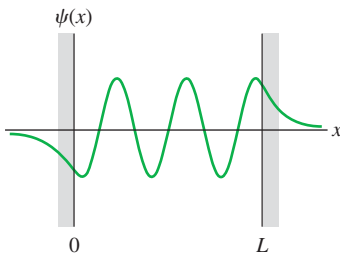
"exponential tails" that extend outside the well into regions that are forbidden by Newtonian mechanics (because in those regions the particle would have negative kinetic energy). We see that there is some probability for finding the particle *outside* the potential well, which would be impossible in classical mechanics. In Section 40.4 we'll discuss an amazing result of this effect.

Example 40.5 | **Outside a finite well**

(a) Show that Eq. (40.40), $\psi(x) = Ce^{\kappa x} + De^{-\kappa x}$, is indeed a solution of the time-independent Schrödinger equation outside a finite well of height U_0. (b) What happens to $\psi(x)$ in the limit $U_0 \to \infty$?

SOLUTION

IDENTIFY and SET UP: In part (a), we try the given function $\psi(x)$ in the time-independent Schrödinger equation for $x < 0$ and for $x > L$, Eq. (40.39). In part (b), we note that in the limit $U_0 \to \infty$ the finite well becomes an *infinite* well, like those we considered in Section 40.2 for a particle in a box. So in this limit the wave functions outside a finite well must reduce to the wave functions outside the box.

EXECUTE: (a) We must show that $\psi(x) = Ce^{\kappa x} + De^{-\kappa x}$ satisfies $d^2\psi(x)/dx^2 = [2m(U_0 - E)/\hbar^2]\psi(x)$. We recall that $(d/du)e^{au} = ae^{au}$ and $(d^2/du^2)e^{au} = a^2e^{au}$; the left-hand side of the Schrödinger equation is then

$$\frac{d^2\psi(x)}{dx^2} = \frac{d^2}{dx^2}(Ce^{\kappa x}) + \frac{d^2}{dx^2}(De^{-\kappa x})$$
$$= C\kappa^2 e^{\kappa x} + D(-\kappa)^2 e^{-\kappa x}$$
$$= \kappa^2(Ce^{\kappa x} + De^{-\kappa x})$$
$$= \kappa^2\psi(x)$$

Since from Eq. (40.40) $\kappa^2 = 2m(U_0 - E)/\hbar^2$, this is equal to the right-hand side of the equation. The equation is satisfied, and $\psi(x)$ is a solution.

(b) As U_0 approaches infinity, κ also approaches infinity. In the region $x < 0$, $\psi(x) = Ce^{\kappa x}$; as $\kappa \to \infty$, $\kappa x \to -\infty$ (since x is negative) and $e^{\kappa x} \to 0$, so the wave function approaches zero for all $x < 0$. Likewise, we can show that the wave function also approaches zero for all $x > L$. This is just what we found in Section 40.2; the wave function for a particle in a box must be zero outside the box.

EVALUATE: Our result in part (b) shows that the infinite square well is a *limiting case* of the finite well. We've seen many cases in Newtonian mechanics where it's important to consider limiting cases (such as Examples 5.11 and 5.13 in Section 5.2). Limiting cases are no less important in quantum mechanics.

Comparing Finite and Infinite Square Wells

Let's continue the comparison of the finite-depth potential well with the infinitely deep well, which we began in Example 40.5. First, because the wave functions for the finite well don't go to zero at $x = 0$ and $x = L$, the wavelength of the sinusoidal part of each wave function is *longer* than it would be with an infinite well. This increase in λ corresponds to a reduced magnitude of momentum $p = h/\lambda$ and therefore a reduced energy. Thus each energy level, including the ground level, is *lower* for a finite well than for an infinitely deep well with the same width.

Second, a well with finite depth U_0 has only a *finite* number of bound states and corresponding energy levels, compared to the *infinite* number for an infinitely deep well. How many levels there are depends on the magnitude of U_0 in comparison with the ground-level energy for the infinitely deep well (IDW), which we call $E_{1-\text{IDW}}$. From Eq. (40.31),

$$E_{1-\text{IDW}} = \frac{\pi^2\hbar^2}{2mL^2} \qquad \text{(ground-level energy, infinitely deep well)} \qquad (40.41)$$

When the well is very deep so U_0 is much larger than $E_{1-\text{IDW}}$, there are many bound states and the energies of the lowest few are nearly the same as the energies for the infinitely deep well. When U_0 is only a few times as large as $E_{1-\text{IDW}}$ there are only a few bound states. (There is always at least *one* bound state, no matter how shallow the well.) As with the infinitely deep well, there is no state with $E = 0$; such a state would violate the uncertainty principle.

40.15 (a) Wave functions for the three bound states for a particle in a finite potential well with depth U_0, for the case $U_0 = 6E_{1-\text{IDW}}$. (Here $E_{1-\text{IDW}}$ is the ground-level energy for an infinite well of the same width.) The horizontal brown line for each wave function corresponds to $\psi = 0$; the vertical placement of these lines indicates the energy of each bound state (compare Fig. 40.11). (b) Energy-level diagram for this system. The energies are expressed both as multiples of $E_{1-\text{IDW}}$ and as fractions of U_0. All energies greater than U_0 are possible; states with $E > U_0$ form a continuum.
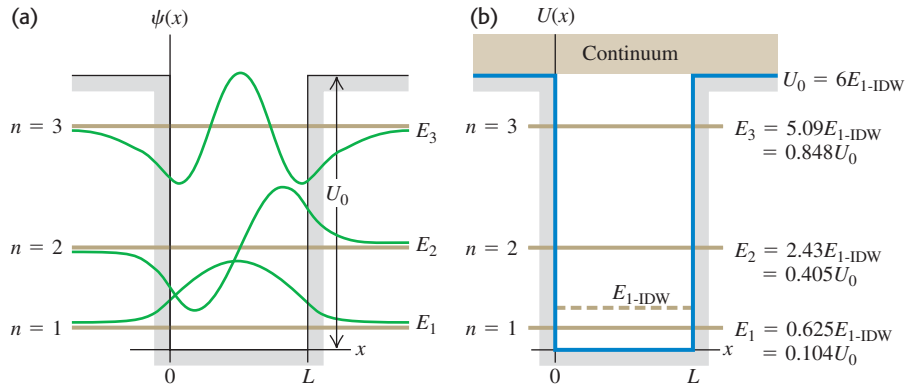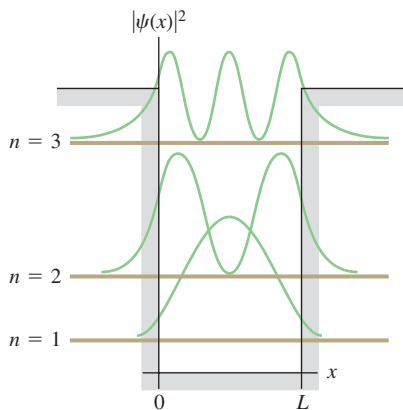

Figure 40.15 shows the case $U_0 = 6E_{1-\text{IDW}}$; for this particular case there are three bound states. In the figure, we express the energy levels both as fractions of the well depth U_0 and as multiples of $E_{1-\text{IDW}}$. Note that if the well were infinitely deep, the lowest three levels, as given by Eq. (40.31), would be $E_{1-\text{IDW}}$, $4E_{1-\text{IDW}}$, and $9E_{1-\text{IDW}}$. Figure 40.15 also shows the wave functions for the three bound states.

It turns out that when U_0 is less than $E_{1-\text{IDW}}$, there is only one bound state. In the limit when U_0 is *much smaller* than $E_{1-\text{IDW}}$ (a very shallow well), the energy of this single state is approximately $E = 0.68U_0$.

Figure 40.16 shows graphs of the probability distributions—that is, the values of $|\psi|^2$—for the wave functions shown in Fig. 40.15a. As with the infinite well, not all positions are equally likely. Unlike the infinite well, there is some probability of finding the particle outside the well in the classically forbidden regions.

There are also states for which E is *greater* than U_0. In these *free-particle states* the particle is not bound but is free to move through all values of x. Any energy E greater than U_0 is possible, so the free-particle states form a *continuum* rather than a discrete set of states with definite energy levels. The free-particle wave functions are sinusoidal both inside and outside the well. The wavelength is shorter inside the well than outside, corresponding to greater kinetic energy inside the well than outside it.

Figure 40.17 shows a graphic demonstration of particles in a *two*-dimensional finite potential well. Example 40.6 describes another application of the square-well potential.

40.16 Probability distribution functions $|\psi(x)|^2$ for the square-well wave functions shown in Fig. 40.15. The horizontal brown line for each wave function corresponds to $|\psi|^2 = 0$.

Example 40.6   **An electron in a finite well**

An electron is trapped in a square well 0.50 nm across (roughly five times a typical atomic diameter). (a) Find the ground-level energy $E_{1-\text{IDW}}$ if the well is infinitely deep. (b) Find the energy levels if the actual well depth U_0 is six times the ground-level energy found in part (a). (c) Find the wavelength of the photon emitted when the electron makes a transition from the $n = 2$ level to the $n = 1$ level. In what region of the electromagnetic spectrum does the photon wavelength lie? (d) If the electron is in the $n = 1$ (ground) level and absorbs a photon, what is the minimum photon energy that will free the electron from the well? In what region of the spectrum does the wavelength of this photon lie?

SOLUTION

IDENTIFY and SET UP: Equation (40.41) gives the ground-level energy $E_{1-\text{IDW}}$ for an infinitely deep well, and Fig. 40.15b shows the energies for a square well with $U_0 = 6E_{1-\text{IDW}}$. The energy of the photon emitted or absorbed in a transition is equal to the difference

in energy between two levels involved in the transition; the photon wavelength is given by $E = hc/\lambda$ (see Chapter 38).

EXECUTE: (a) From Eq. (40.41),

$$E_{1-\text{IDW}} = \frac{\pi^2 \hbar^2}{2mL^2} = \frac{\pi^2 (1.055 \times 10^{-34} \text{ J} \cdot \text{s})^2}{2(9.11 \times 10^{-31} \text{ kg})(0.50 \times 10^{-9} \text{ m})^2}$$

$$= 2.4 \times 10^{-19} \text{ J} = 1.5 \text{ eV}$$

(b) We have $U_0 = 6E_{1-\text{IDW}} = 6(1.5 \text{ eV}) = 9.0 \text{ eV}$. We can read off the energy levels from Fig. 40.15b:

$$E_1 = 0.625E_{1-\text{IDW}} = 0.625(1.5 \text{ eV}) = 0.94 \text{ eV}$$

$$E_2 = 2.43E_{1-\text{IDW}} = 2.43(1.5 \text{ eV}) = 3.6 \text{ eV}$$

$$E_3 = 5.09E_{1-\text{IDW}} = 5.09(1.5 \text{ eV}) = 7.6 \text{ eV}$$

(c) The photon energy and wavelength for the $n = 2$ to $n = 1$ transition are

$$E_2 - E_1 = 3.6 \text{ eV} - 0.94 \text{ eV} = 2.7 \text{ eV}$$

$$\lambda = \frac{hc}{E} = \frac{(4.136 \times 10^{-15} \text{ eV} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{2.7 \text{ eV}}$$

$$= 460 \text{ nm}$$

in the blue region of the visible spectrum.

(d) We see from Fig. 40.15b that the minimum energy needed to free the electron from the well from the $n = 1$ level is $U_0 - E_1 = 9.0 \text{ eV} - 0.94 \text{ eV} = 8.1 \text{ eV}$, which is three times the 2.7-eV photon energy found in part (c). Hence the corresponding photon wavelength is one-third of 460 nm, or (to two significant figures) 150 nm, which is in the ultraviolet region of the spectrum.
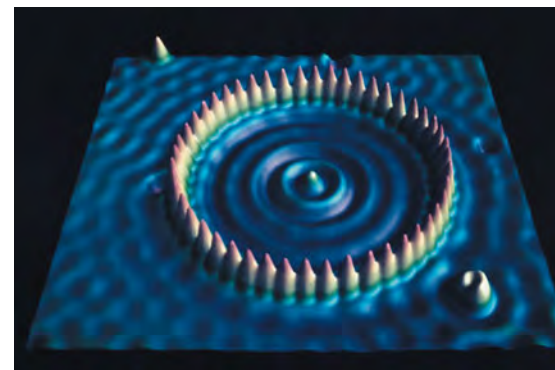
EVALUATE: As a check, you can also calculate the bound-state energies by using the formulas $E_1 = 0.104U_0$, $E_2 = 0.405U_0$, and $E_3 = 0.848U_0$ given in Fig. 40.15b. As an additional check, note that the first three energy levels of an infinitely deep well of the same width are $E_{1-\text{IDW}} = 1.5 \text{ eV}$, $E_{2-\text{IDW}} = 4E_{1-\text{IDW}} = 6.0 \text{ eV}$, and $E_{3-\text{IDW}} = 9E_{1-\text{IDW}} = 13.5 \text{ eV}$. The energies we found in part (b) are less than these values: As we mentioned earlier, the finite depth of the well lowers the energy levels compared to the levels for an infinitely deep well.

One application of these ideas is to *quantum dots,* which are nanometer-sized particles of a semiconductor such as cadmium selenide (CdSe). An electron within a quantum dot behaves much like a particle in a finite potential well of width L equal to the size of the dot. When quantum dots are illuminated with ultraviolet light, the electrons absorb the ultraviolet photons and are excited into high energy levels, such as the $n = 3$ level described in this example. If the electron returns to the ground level ($n = 1$) in two or more steps (for example, from $n = 3$ to $n = 2$ and from $n = 2$ to $n = 1$), one of the steps will involve emitting a visible-light photon, as we have calculated here. (We described this process of *fluorescence* in Section 39.3.) Increasing the value of L decreases the energies of the levels and hence the spacing between them, and thus decreases the energy and increases the wavelength of the emitted photons. The photograph that opens this chapter shows quantum dots of different sizes in solution: Each emits a characteristic wavelength that depends on the dot size. Quantum dots can be injected into living tissue and their fluorescent glow used as a tracer for biological research and for medicine. They may also be the key to a new generation of lasers and ultrafast computers.

Test Your Understanding of Section 40.3 Suppose that the width of the finite potential well shown in Fig. 40.15 is reduced by one-half. How must the value of U_0 change so that there are still just three bound energy levels whose energies are the fractions of U_0 shown in Fig. 40.15b? U_0 must: (i) increase by a factor of four; (ii) increase by a factor of two; (iii) remain the same; (iv) decrease by a factor of one-half; (v) decrease by a factor of one-fourth.

40.4 Potential Barriers and Tunneling

A **potential barrier** is the opposite of a potential well; it is a potential-energy function with a *maximum.* Figure 40.18 shows an example. In classical Newtonian mechanics, if a particle (such as a roller coaster) is located to the left of the barrier (which might be a hill), and if the total mechanical energy of the system is E_1, the particle cannot move farther to the right than $x = a$. If it did, the potential energy U would be greater than the total energy E and the kinetic energy $K = E - U$ would be negative. This is impossible in classical mechanics since $K = \frac{1}{2}mv^2$ can never be negative.

A quantum-mechanical particle behaves differently: If it encounters a barrier like the one in Fig. 40.18 and has energy less than E_2, it *may* appear on the other side. This phenomenon is called *tunneling.* In quantum-mechanical tunneling, unlike macroscopic, mechanical tunneling, the particle does not actually push through the barrier and loses no energy in the process.

Tunneling Through a Rectangular Barrier

To understand how tunneling can occur, let's look at the potential-energy function $U(x)$ shown in Fig. 40.19. It's like Fig. 40.13 turned upside-down; the potential energy is zero everywhere except in the range $0 \leq x \leq L$, where it has the value U_0. This might represent a simple model for the potential energy of an

40.17 To make this image, 48 iron atoms (shown as yellow peaks) were placed in a circle on a copper surface. The "elevation" at each point inside the circle indicates the electron density within the circle. The standing-wave pattern is very similar to the probability distribution function for a particle in a one-dimensional finite potential well. (This image was made with a scanning tunneling microscope, discussed in Section 40.4.)


MasteringPHYSICS

PhET: Quantum Tunneling and Wave Packets
**ActivPhysics 20.4:** Potential Barriers

40.18 A potential-energy barrier. According to Newtonian mechanics, if the total energy of the system is E_1, a particle to the left of the barrier can go no farther than $x = a$. If the total energy is greater than E_2, the particle can pass over the barrier.
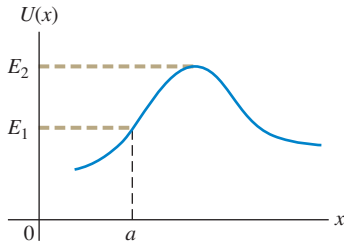
40.19 A rectangular potential-energy barrier with width L and height U_0. According to Newtonian mechanics, if the total energy E is less than U_0, a particle cannot pass over this barrier but is confined to the side where it starts.
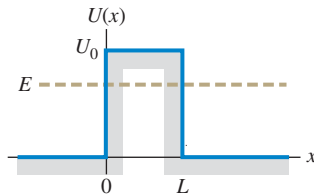
40.20 A possible wave function for a particle tunneling through the potential-energy barrier shown in Fig. 40.19.
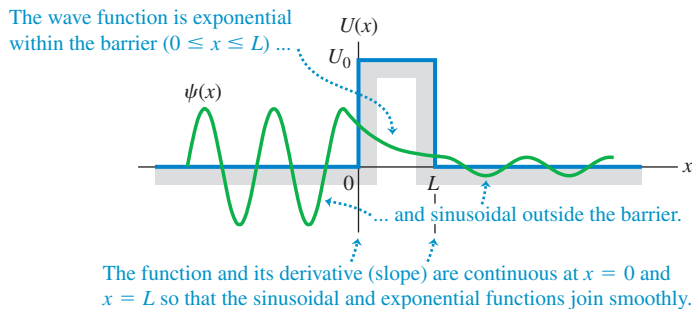
electron in the presence of two slabs of metal separated by an air gap of thickness L. The potential energy is lower within either slab than in the gap between them.

Let's consider solutions of the Schrödinger equation for this potential-energy function for the case in which E is less than U_0. We can use our results from Section 40.3. In the regions $x < 0$ and $x > L$, where $U = 0$, the solution is sinusoidal and is given by Eq. (40.38). Within the barrier ($0 \le x \le L$), $U = U_0$ and the solution is exponential as in Eq. (40.40). Just as with the finite potential well, the functions have to join smoothly at the boundary points $x = 0$ and $x = L$, which means that both $\psi(x)$ and $d\psi(x)/dx$ have to be continuous at these points.

These requirements lead to a wave function like the one shown in Fig. 40.20. The function is *not* zero inside the barrier (the region forbidden by Newtonian mechanics). Even more remarkable, a particle that is initially to the *left* of the barrier has some probability of being found to the *right* of the barrier. How great this probability is depends on the width L of the barrier and the particle's energy E in comparison with the barrier height U_0. The **tunneling probability** T that the particle gets through the barrier is proportional to the square of the ratio of the amplitudes of the sinusoidal wave functions on the two sides of the barrier. These amplitudes are determined by matching wave functions and their derivatives at the boundary points, a fairly involved mathematical problem. When T is much smaller than unity, it is given approximately by

$$T = Ge^{-2\kappa L} \text{ where } G = 16\frac{E}{U_0}\left(1 - \frac{E}{U_0}\right) \text{ and } \kappa = \frac{\sqrt{2m(U_0 - E)}}{\hbar} \quad (40.42)$$

$$\text{(probability of tunneling)}$$

The probability decreases rapidly with increasing barrier width L. It also depends critically on the energy difference $U_0 - E$, which in Newtonian physics is the additional kinetic energy the particle would need to be able to climb over the barrier.

Example 40.7 **Tunneling through a barrier**

A 2.0-eV electron encounters a barrier 5.0 eV high. What is the probability that it will tunnel through the barrier if the barrier width is (a) 1.00 nm and (b) 0.50 nm?

SOLUTION

IDENTIFY and SET UP: This problem uses the ideas of tunneling through a rectangular barrier, as in Figs. 40.19 and 40.20. Our target variable is the tunneling probability T in Eq. (40.42), which we evaluate for the given values $E = 2.0$ eV (electron energy), $U = 5.0$ eV (barrier height), $m = 9.11 \times 10^{-31}$ kg (mass of the electron), and $L = 1.00$ nm or 0.50 nm (barrier width).

EXECUTE: First we evaluate G and κ in Eq. (40.42), using $E = 2.0$ eV:

$$G = 16\left(\frac{2.0 \text{ eV}}{5.0 \text{ eV}}\right)\left(1 - \frac{2.0 \text{ eV}}{5.0 \text{ eV}}\right) = 3.8$$

$$U_0 - E = 5.0 \text{ eV} - 2.0 \text{ eV} = 3.0 \text{ eV} = 4.8 \times 10^{-19} \text{ J}$$

$$\kappa = \frac{\sqrt{2(9.11 \times 10^{-31} \text{ kg})(4.8 \times 10^{-19} \text{ J})}}{1.055 \times 10^{-34} \text{ J} \cdot \text{s}} = 8.9 \times 10^9 \text{ m}^{-1}$$

(a) When $L = 1.00$ nm $= 1.00 \times 10^{-9}$ m, $2\kappa L = 2(8.9 \times 10^9 \text{ m}^{-1})(1.00 \times 10^{-9} \text{ m}) = 17.8$ and $T = Ge^{-2\kappa L} = 3.8e^{-17.8} = 7.1 \times 10^{-8}$.

(b) When $L = 0.50$ nm, one-half of 1.00 nm, $2\kappa L$ is one-half of 17.8, or 8.9. Hence $T = 3.8e^{-8.9} = 5.2 \times 10^{-4}$.

EVALUATE: Halving the width of this barrier increases the tunneling probability T by a factor of $(5.2 \times 10^{-4})/(7.1 \times 10^{-8}) = 7.3 \times 10^3$, or nearly ten thousand. The tunneling probability is an *extremely* sensitive function of the barrier width.

(a)

(b)
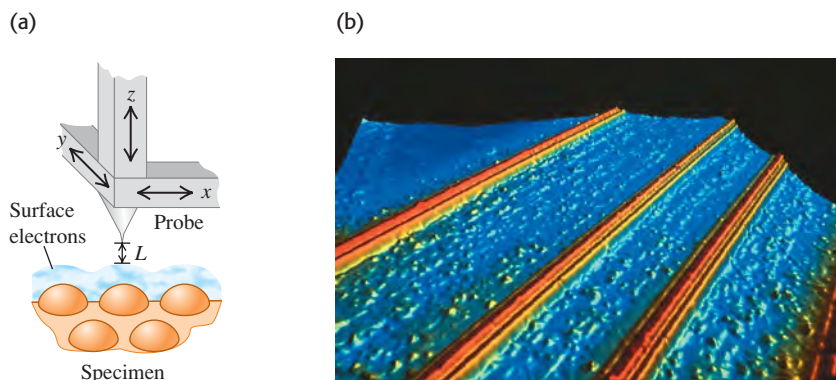
40.21 (a) Schematic diagram of the probe of a scanning tunneling microscope (STM). As the sharp conducting probe is scanned across the surface in the x- and y-directions, it is also moved in the z-direction to maintain a constant tunneling current. The changing position of the probe is recorded and used to construct an image of the surface. (b) This colored STM image shows "quantum wires": thin strips, just 10 atoms wide, of a conductive rare-earth silicide atop a silicon surface. Such quantum wires may one day be the basis of ultraminiaturized circuits.

Applications of Tunneling

Tunneling has a number of practical applications, some of considerable importance. When you twist two copper wires together or close the contacts of a switch, current passes from one conductor to the other despite a thin layer of nonconducting copper oxide between them. The electrons tunnel through this thin insulating layer. A *tunnel diode* is a semiconductor device in which electrons tunnel through a potential barrier. The current can be switched on and off very quickly (within a few picoseconds) by varying the height of the barrier. A *Josephson junction* consists of two superconductors separated by an oxide layer a few atoms (1 to 2 nm) thick. Electron pairs in the superconductors can tunnel through the barrier layer, giving such a device unusual circuit properties. Josephson junctions are useful for establishing precise voltage standards and measuring tiny magnetic fields, and they play a crucial role in the developing field of quantum computing.

The *scanning tunneling microscope* (STM) uses electron tunneling to create images of surfaces down to the scale of individual atoms. An extremely sharp conducting needle is brought very close to the surface, within 1 nm or so (Fig. 40.21a). When the needle is at a positive potential with respect to the surface, electrons can tunnel through the surface potential-energy barrier and reach the needle. As Example 40.7 shows, the tunneling probability and hence the tunneling current are very sensitive to changes in the width L of the barrier (the distance between the surface and the needle tip). In one mode of operation the needle is scanned across the surface and at the same time is moved perpendicular to the surface to maintain a constant tunneling current. The needle motion is recorded, and after many parallel scans, an image of the surface can be reconstructed. Extremely precise control of needle motion, including isolation from vibration, is essential. Figure 40.21b shows an STM image. (Figure 40.17 is also an STM image.)
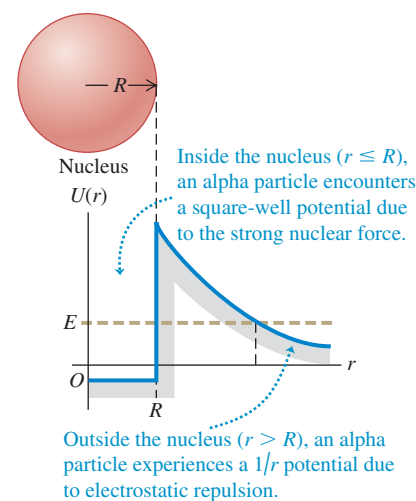
Tunneling is also of great importance in nuclear physics. A fusion reaction can occur when two nuclei tunnel through the barrier caused by their electrical repulsion and approach each other closely enough for the attractive nuclear force to cause them to fuse. Fusion reactions occur in the cores of stars, including the sun; without tunneling, the sun wouldn't shine. The emission of alpha particles from unstable nuclei such as radium also involves tunneling. An alpha particle is a cluster of two protons and two neutrons (the same as a nucleus of the most common form of helium). Such clusters form naturally within larger atomic nuclei. An alpha particle trying to escape from a nucleus encounters a potential barrier that results from the combined effect of the attractive nuclear force and the electrical repulsion of the remaining part of the nucleus (Fig. 40.22). The alpha particle can escape only by tunneling through this barrier. Depending on the barrier height and width for a given kind of alpha-emitting nucleus, the tunneling probability can be low or high, and the alpha-emitting material will have low or high radioactivity. Recall from Section 39.2 that Ernest Rutherford used alpha particles

Application Electron Tunneling in Enzymes
Protein molecules play essential roles as enzymes in living organisms. Enzymes like the one shown here are large molecules, and in many cases their function depends on the ability of electrons to tunnel across the space that separates one part of the molecule from another. Without tunneling, life as we know it would be impossible!
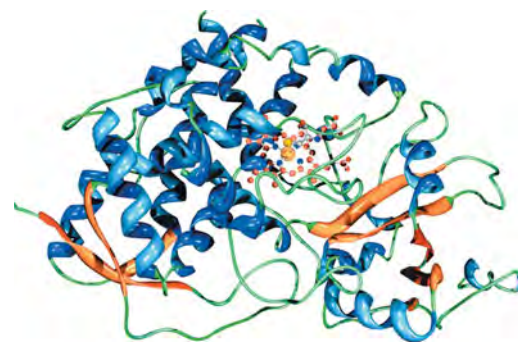
40.22 Approximate potential-energy function for an alpha particle interacting with a nucleus of radius R. If an alpha particle inside the nucleus has energy E greater than zero, it can tunnel through the barrier and escape from the nucleus.

Nucleus

$U(r)$

— R →

Inside the nucleus ($r \le R$), an alpha particle encounters a square-well potential due to the strong nuclear force.

E

O

R

r

Outside the nucleus ($r > R$), an alpha particle experiences a $1/r$ potential due to electrostatic repulsion.

from a radioactive source to discover the atomic nucleus. Although Rutherford did not know it, tunneling by these alpha particles made his experiments possible! We'll learn more about alpha decay in Chapter 43.

Test Your Understanding of Section 40.4 Is it possible for a particle undergoing tunneling to be found *within* the barrier rather than on either side of it? ❙

40.5 The Harmonic Oscillator

Systems that *oscillate* are of tremendous importance in the physical world, from the oscillations of your eardrums in response to a sound wave to the vibrations of the ground caused by an earthquake. Oscillations are equally important on the microscopic scale where quantum effects dominate. The molecules of the air around you can be set into vibration when they collide with each other, the protons and neutrons in an excited atomic nucleus can oscillate in opposite directions, and a microwave oven transfers energy to food by making water molecules in the food flip back and forth. In this section we'll look at the solutions of the Schrödinger equation for the simplest kind of vibrating system, the quantum-mechanical harmonic oscillator.

40.23 Potential-energy function for the harmonic oscillator. In Newtonian mechanics the amplitude A is related to the total energy E by $E = \frac{1}{2}k'A^2$, and the particle is restricted to the range from $x = -A$ to $x = A$. In quantum mechanics the particle can be found at $x > A$ or $x < -A$.
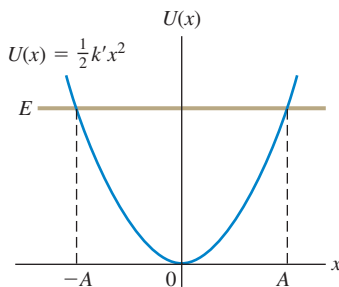
As we learned in Chapter 14, a **harmonic oscillator** is a particle with mass m that moves along the x-axis under the influence of a conservative force $F_x = -k'x$. The constant k' is called the *force constant*. (In Chapter 14 we used the symbol k for the force constant. In this section we'll use the symbol k' instead to minimize confusion with the wave number $k = 2\pi/\lambda$.) The force is proportional to the particle's displacement x from its equilibrium position, $x = 0$. The corresponding potential-energy function is $U = \frac{1}{2}k'x^2$ (Fig. 40.23). In Newtonian mechanics, when the particle is displaced from equilibrium, it undergoes sinusoidal motion with frequency $f = (1/2\pi)(k'/m)^{1/2}$ and angular frequency $\omega = 2\pi f = (k'/m)^{1/2}$. The amplitude (that is, the maximum displacement from equilibrium) of these Newtonian oscillations is A, which is related to the energy E of the oscillator by $E = \frac{1}{2}k'A^2$.

Let's make an enlightened guess about the energy levels of a quantum-mechanical harmonic oscillator. In classical physics an electron oscillating with angular frequency ω emits electromagnetic radiation with that same angular frequency. It's reasonable to guess that when an excited quantum-mechanical harmonic oscillator with angular frequency $\omega = (k'/m)^{1/2}$ (according to Newtonian mechanics, at least) makes a transition from one energy level to a lower level, it would emit a photon with this same angular frequency ω. The energy of such a photon is $hf = (h/2\pi)(\omega/2\pi) = \hbar\omega$. So we would expect that the spacing between adjacent energy levels of the harmonic oscillator would be

$$ hf = \hbar\omega = \hbar\sqrt{\frac{k'}{m}} \qquad (40.43) $$

That's the same spacing between energy levels that Planck assumed in deriving his radiation law (see Section 39.5). It was a good assumption; as we'll see, the energy levels are in fact half-integer $\left(\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots\right)$ multiples of $\hbar\omega$.

Wave Functions, Boundary Conditions, and Energy Levels

We'll begin our quantum-mechanical analysis of the harmonic oscillator by writing down the one-dimensional time-independent Schrödinger equation, Eq. (40.23), with $\frac{1}{2}k'x^2$ in place of U:

$$ -\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + \frac{1}{2}k'x^2\psi(x) = E\psi(x) \qquad \begin{array}{l}\text{(Schrödinger equation for} \\ \text{the harmonic oscillator)}\end{array} \qquad (40.44) $$

The solutions of this equation are wave functions for the physically possible states of the system.

In the discussion of square-well potentials in Section 40.2 we found that the energy levels are determined by boundary conditions at the walls of the well. However, the harmonic-oscillator potential has no walls as such; what, then, are the appropriate boundary conditions? Classically, $|x|$ cannot be greater than the amplitude A given by $E = \frac{1}{2}k'A^2$. Quantum mechanics does allow some penetration into classically forbidden regions, but the probability decreases as that penetration increases. Thus the wave functions must approach zero as $|x|$ grows large.

Satisfying the requirement that $\psi(x) \to 0$ as $|x| \to \infty$ is not as trivial as it may seem. To see why this is, let's rewrite Eq. (40.44) in the form

$$\frac{d^2\psi(x)}{dx^2} = \frac{2m}{\hbar^2}\left(\tfrac{1}{2}k'x^2 - E\right)\psi(x) \qquad (40.45)$$

Equation (40.45) shows that when x is large enough (either positive or negative) to make the quantity $\left(\frac{1}{2}k'x^2 - E\right)$ positive, the function $\psi(x)$ and its second derivative $d^2\psi(x)/dx^2$ have the same sign. Figure 40.24 shows four possible kinds of behavior of $\psi(x)$ beginning at a point where x is greater than the classical amplitude A, so that $\frac{1}{2}k'x^2 - \frac{1}{2}k'A^2 = \frac{1}{2}k'x^2 - E > 0$. Let's look at these four cases more closely. Note that if $\psi(x)$ is positive as shown in Fig. 40.24, Eq. (40.45) tells us that $d^2\psi(x)/dx^2$ is also positive and the function is *concave upward*. Note also that $d^2\psi(x)/dx^2$ is the rate of change of the *slope* of $\psi(x)$; this will help us understand how our four possible wave functions behave.

- *Curve a:* The slope of $\psi(x)$ is positive at point x. Since $d^2\psi(x)/dx^2 > 0$, the function curves upward increasingly steeply and goes to infinity. This violates the boundary condition that $\psi(x) \to 0$ as $|x| \to \infty$, so this isn't a viable wave function.
- *Curve b:* The slope of $\psi(x)$ is negative at point x, and $d^2\psi(x)/dx^2$ has a large positive value. Hence the slope changes rapidly from negative to positive and keeps on increasing—so, again, the wave function goes to infinity. This wave function isn't viable either.
- *Curve c:* As for curve b, the slope is negative at point x. However, $d^2\psi(x)/dx^2$ now has a *small* positive value, so the slope increases only gradually as $\psi(x)$ decreases to zero and crosses over to negative values. Equation (40.45) tells us that once $\psi(x)$ becomes negative, $d^2\psi(x)/dx^2$ also becomes negative. Hence the curve becomes concave *downward* and heads for *negative* infinity. This wave function, too, fails to satisfy the requirement that $\psi(x) \to 0$ as $|x| \to \infty$ and thus isn't viable.
- *Curve d:* If the slope of $\psi(x)$ at point x is negative, and the positive value of $d^2\psi(x)/dx^2$ at this point is neither too large nor too small, the curve bends just enough to glide in asymptotically to the x-axis. In this case $\psi(x)$, $d\psi(x)/dx$, and $d^2\psi(x)/dx^2$ all approach zero at large x. This case offers the only hope of satisfying the boundary condition that $\psi(x) \to 0$ as $|x| \to \infty$, and it occurs only for certain very special values of the energy E.

This qualitative discussion suggests how the boundary conditions as $|x| \to \infty$ determine the possible energy levels for the quantum-mechanical harmonic oscillator. It turns out that these boundary conditions are satisifed only if the energy E is equal to one of the values E_n, given by the simple formula

$$E_n = (n + \tfrac{1}{2})\hbar\sqrt{\frac{k'}{m}} = (n + \tfrac{1}{2})\hbar\omega \quad (n = 0, 1, 2, \dots) \qquad (40.46)$$

(energy levels, harmonic oscillator)

where n is the quantum number identifying each state and energy level. Note that the ground level of energy $E_0 = \frac{1}{2}\hbar\omega$ is denoted by $n = 0$, *not* $n = 1$.

40.24 Possible behaviors of harmonic-oscillator wave functions in the region $\frac{1}{2}k'x^2 > E$. In this region, $\psi(x)$ and $d^2\psi(x)/dx^2$ have the same sign. The curve is concave upward when $d^2\psi(x)/dx^2$ is positive and concave downward when $d^2\psi(x)/dx^2$ is negative.
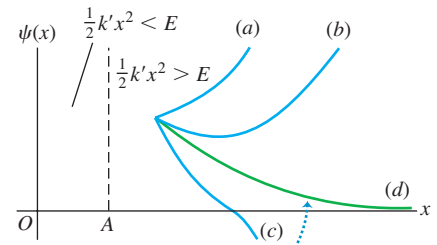
Only curve d, which approaches the x-axis asymptotically for large x, is an acceptable wave function for this system.

40.25 Energy levels for the harmonic oscillator. The spacing between any two adjacent levels is $\Delta E = \hbar\omega$. The energy of the ground level is $E_0 = \frac{1}{2}\hbar\omega$.

$U(x)$

$E_5 = \frac{11}{2}\hbar\omega$

$E_4 = \frac{9}{2}\hbar\omega$

$E_3 = \frac{7}{2}\hbar\omega$

$E_2 = \frac{5}{2}\hbar\omega$

$\Delta E = \hbar\omega$ $E_1 = \frac{3}{2}\hbar\omega$

$E_0 = \frac{1}{2}\hbar\omega$
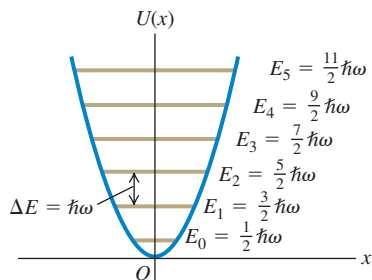
Equation (40.46) confirms our guess [(Eq. 40.43)] that adjacent energy levels are separated by a constant interval of $\hbar\omega = hf$, as Planck assumed in 1900. There are infinitely many levels; this shouldn't be surprising because we are dealing with an infinitely deep potential well. As $|x|$ increases, $U = \frac{1}{2}k'x^2$ increases without bound.

Figure 40.25 shows the lowest six energy levels and the potential-energy function $U(x)$. For each level n, the value of $|x|$ at which the horizontal line representing the total energy E_n intersects $U(x)$ gives the amplitude A_n of the corresponding Newtonian oscillator.

Example 40.8 | **Vibration in a crystal**

A sodium atom of mass 3.82×10^{-26} kg vibrates within a crystal. The potential energy increases by 0.0075 eV when the atom is displaced 0.014 nm from its equilibrium position. Treat the atom as a harmonic oscillator. (a) Find the angular frequency of the oscillations according to Newtonian mechanics. (b) Find the spacing (in electron volts) of adjacent vibrational energy levels according to quantum mechanics. (c) What is the wavelength of a photon emitted as the result of a transition from one level to the next lower level? In what region of the electromagnetic spectrum does this lie?

SOLUTION

IDENTIFY and SET UP: We'll find the force constant k' from the expression $U = \frac{1}{2}k'x^2$ for potential energy. We'll then find the angular frequency $\omega = (k'/m)^{1/2}$ and use this in Eq. (40.46) to find the spacing between adjacent energy levels. We'll calculate the wavelength of the emitted photon as in Example 40.6.

EXECUTE: We are given that $U = 0.0075$ eV $= 1.2 \times 10^{-21}$ J when $x = 0.014 \times 10^{-9}$ m, so we can solve $U = \frac{1}{2}k'x^2$ for k':

$$k' = \frac{2U}{x^2} = \frac{2(1.2 \times 10^{-21} \text{ J})}{(0.014 \times 10^{-9} \text{ m})^2} = 12.2 \text{ N/m}$$

(a) The Newtonian angular frequency is

$$\omega = \sqrt{\frac{k'}{m}} = \sqrt{\frac{12.2 \text{ N/m}}{3.82 \times 10^{-26} \text{ kg}}} = 1.79 \times 10^{13} \text{ rad/s}$$

(b) From Eq. (40.46) and Fig. 40.25, the spacing between adjacent energy levels is

$$\hbar\omega = (1.054 \times 10^{-34} \text{ J}\cdot\text{s})(1.79 \times 10^{13} \text{ s}^{-1})$$

$$= 1.88 \times 10^{-21} \text{ J}\left(\frac{1 \text{ eV}}{1.602 \times 10^{-19} \text{ J}}\right) = 0.0118 \text{ eV}$$

(c) The energy E of the emitted photon is equal to the energy lost by the oscillator in the transition, 0.0118 eV. Then

$$\lambda = \frac{hc}{E} = \frac{(4.136 \times 10^{-15} \text{ eV}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{0.0118 \text{ eV}}$$

$$= 1.05 \times 10^{-4} \text{ m} = 105 \text{ } \mu\text{m}$$

This photon wavelength is in the infrared region of the spectrum.

EVALUATE: This example shows us that interatomic force constants are a few newtons per meter, about the same as those of household springs or spring-based toys such as the Slinky. It also suggests that we can learn about the vibrations of molecules by measuring the radiation that they emit in transitioning to a lower vibrational state. We will explore this idea further in Chapter 42.

Mastering PHYSICS

ActivPhysics 20.1.6: Potential Energy Diagrams, Question 6

**Comparing Quantum and Newtonian Oscillators**

The wave functions for the levels $n = 0, 1, 2, \ldots$ of the harmonic oscillator are called *Hermite functions;* they aren't encountered in elementary calculus courses but are well known to mathematicians. Each Hermite function is an exponential function multiplied by a polynomial in x. The harmonic-oscillator wave function corresponding to $n = 0$ and $E = E_0$ (the ground level) is

$$\psi(x) = Ce^{-\sqrt{mk'}\, x^2/2\hbar} \tag{40.47}$$

The constant C is chosen to normalize the function—that is, to make $\int_{-\infty}^{\infty} |\psi|^2 \, dx = 1$. (We're using C rather than A as a normalization constant in this section, since we've already appropriated the symbol A to denote the Newtonian amplitude of a harmonic oscillator.) You can find C using the following result from integral tables:

$$\int_{-\infty}^{\infty} e^{-a^2x^2} dx = \frac{\sqrt{\pi}}{a}$$

40.26 The first four wave functions for the harmonic oscillator. The amplitude A of a Newtonian oscillator with the same total energy is shown for each. Each wave function penetrates somewhat into the classically forbidden regions $|x| > A$. The total number of finite maxima and minima for each function is $n + 1$, one more than the quantum number.
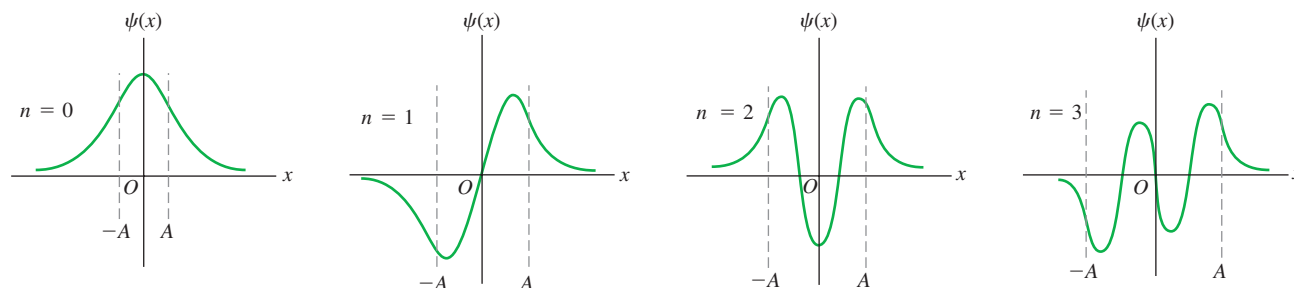
To confirm that $\psi(x)$ as given by Eq. (40.47) really *is* a solution of the Schrödinger equation for the harmonic oscillator, we invite you to calculate the second derivative of this wave function, substitute it into Eq. (40.44), and verify that the equation is satisfied if the energy E is equal to $E_0 = \frac{1}{2}\hbar\omega$ (see Exercise 40.38). It's a little messy, but the result is satisfying and worth the effort.

Figure 40.26 shows the the first four harmonic-oscillator wave functions. Each graph also shows the amplitude A of a Newtonian harmonic oscillator with the same energy—that is, the value of A determined from

$$\frac{1}{2}k'A^2 = \left(n + \frac{1}{2}\right)\hbar\omega \qquad (40.48)$$

In each case there is some penetration of the wave function into the regions $|x| > A$ that are forbidden by Newtonian mechanics. This is similar to the effect that we noted in Section 40.3 for a particle in a finite square well.

Figure 40.27 shows the probability distributions $|\psi(x)|^2$ for these same states. Each graph also shows the probability distribution determined from Newtonian physics, in which the probability of finding the particle near a randomly chosen point is inversely proportional to the particle's speed at that point. If we average out the wiggles in the quantum-mechanical probability curves, the results for $n > 0$ resemble the Newtonian predictions. This agreement improves with increasing n; Fig. 40.28 shows the classical and quantum-mechanical probability functions for $n = 10$. Notice that the spacing between zeros of $|\psi(x)|^2$ in Fig. 40.28 increases with increasing distance from $x = 0$. This makes sense from the Newtonian perspective: As a particle moves away from $x = 0$, its kinetic energy K and the magnitude p of its momentum both decrease. Thinking quantum-mechanically, this means that the wavelength $\lambda = h/p$ increases, so the spacing between zeros of $\psi(x)$ (and hence of $|\psi(x)|^2$) also increases.

In the Newtonian analysis of the harmonic oscillator the minimum energy is zero, with the particle at rest at its equilibrium position $x = 0$. This is not possible in quantum mechanics; no solution of the Schrödinger equation has $E = 0$ and satisfies the boundary conditions. Furthermore, if there were such a state, it

40.27 Probability distribution functions $|\psi(x)|^2$ for the harmonic-oscillator wave functions shown in Fig. 40.26. The amplitude A of the Newtonian motion with the same energy is shown for each. The blue lines show the corresponding probability distributions for the Newtonian motion. As n increases, the averaged-out quantum-mechanical functions resemble the Newtonian curves more and more.
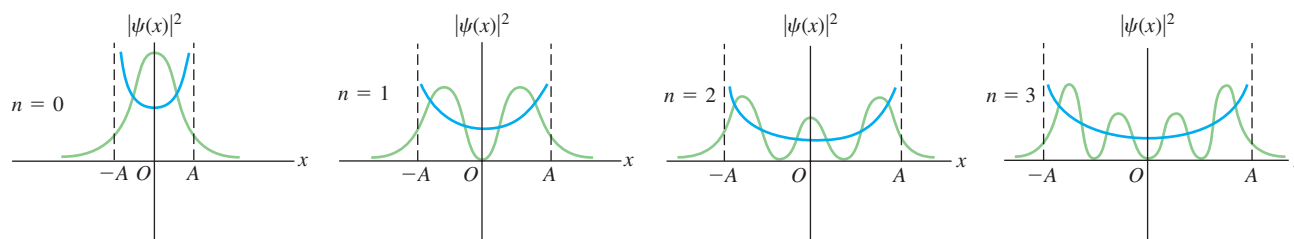
**40.28** Newtonian and quantum-mechanical probability distribution functions for a harmonic oscillator for the state $n = 10$. The Newtonian amplitude A is also shown.

The larger the value of n, the more closely the quantum-mechanical probability distribution (green) matches the Newtonian probability distribution (blue).
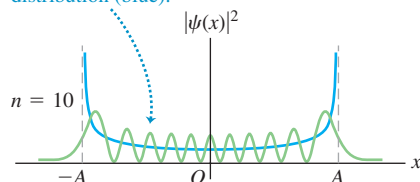
40.29 A potential-energy function describing the interaction of two atoms in a diatomic molecule. The distance r is the separation between the centers of the atoms, and the equilibrium separation is $r = r_0$. The energy needed to dissociate the molecule is U_∞.
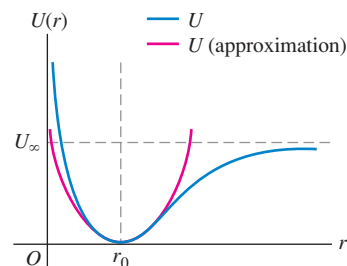
When r is near r_0, the potential-energy curve is approximately parabolic (as shown by the red curve) and the system behaves approximately like a harmonic oscillator.

would violate the Heisenberg uncertainty principle because there would be no uncertainty in either position or momentum. The energy must be at least $\frac{1}{2}\hbar\omega$ for the system to conform to the uncertainty principle. To see qualitatively why this is so, consider a Newtonian oscillator with total energy $\frac{1}{2}\hbar\omega$. We can find the amplitude A and the maximum velocity just as we did in Section 14.3. When the particle is at its maximum displacement $(x = \pm A)$ and instantaneously at rest, $K = 0$ and $E = U = \frac{1}{2}k'A^2$. When the particle is at equilibrium $(x = 0)$ and moving at its maximum speed, $U = 0$ and $E = K = \frac{1}{2}mv_{\text{max}}^2$. Setting $E = \frac{1}{2}\hbar\omega$, we find

$$E = \tfrac{1}{2}k'A^2 = \tfrac{1}{2}\hbar\omega = \tfrac{1}{2}\hbar\left(\frac{k'}{m}\right)^{1/2} \qquad \text{so} \qquad A = \frac{\hbar^{1/2}}{k'^{1/4}m^{1/4}}$$

$$E = \tfrac{1}{2}mv_{\text{max}}^2 = \tfrac{1}{2}k'A^2 \qquad \text{so} \qquad v_{\text{max}} = A\left(\frac{k'}{m}\right)^{1/2} = \frac{\hbar^{1/2}k'^{1/4}}{m^{3/4}}$$

The maximum *momentum* of the particle is

$$p_{\text{max}} = mv_{\text{max}} = \hbar^{1/2}k'^{1/4}m^{1/4}$$

Here's where the Heisenberg uncertainty principle comes in. It turns out that the uncertainties in the particle's position and momentum (calculated as standard deviations) are, respectively, $\Delta x = A/\sqrt{2} = A/2^{1/2}$ and $\Delta p_x = p_{\text{max}}/\sqrt{2} = p_{\text{max}}/2^{1/2}$. Then the product of the two uncertainties is

$$\Delta x\, \Delta p_x = \left(\frac{\hbar^{1/2}}{2^{1/2}\,k'^{1/4}\,m^{1/4}}\right)\left(\frac{\hbar^{1/2}\,k'^{1/4}\,m^{1/4}}{2^{1/2}}\right) = \frac{\hbar}{2}$$

This product equals the minimum value allowed by Eq. (39.29), $\Delta x\, \Delta p_x \geq \hbar/2$, and thus satisfies the uncertainty principle. If the energy had been less than $\frac{1}{2}\hbar\omega$, the product $\Delta x\, \Delta p_x$ would have been less than $\hbar/2$, and the uncertainty principle would have been violated.

Even when a potential-energy function isn't precisely parabolic in shape, we may be able to approximate it by the harmonic-oscillator potential for sufficiently small displacements from equilibrium. Figure 40.29 shows a typical potential-energy function for an interatomic force in a molecule. At large separations the curve of $U(r)$ versus r levels off, corresponding to the absence of force at great distances. But the curve is approximately parabolic near the minimum of $U(r)$ (the equilibrium separation of the atoms). Near equilibrium the molecular vibration is approximately simple harmonic with energy levels given by Eq. (40.46), as we assumed in Example 40.8.

Test Your Understanding of Section 40.5 A quantum-mechanical system initially in its ground level absorbs a photon and ends up in the first excited state. The system then absorbs a second photon and ends up in the second excited state. For which of the following systems does the second photon have a longer wavelength than the first one? (i) a harmonic oscillator; (ii) a hydrogen atom; (iii) a particle in a box.

Wave functions: The wave function for a particle contains all of the information about that particle. If the particle moves in one dimension in the presence of a potential energy function $U(x)$, the wave function $\Psi(x, t)$ obeys the one-dimensional Schrödinger equation. (For a *free* particle on which no forces act, $U(x) = 0$.) The quantity $|\Psi(x, t)|^2$, called the probability distribution function, determines the relative probability of finding a particle near a given position at a given time. If the particle is in a state of definite energy, called a stationary state, $\Psi(x, t)$ is a product of a function $\psi(x)$ that depends only on spatial coordinates and a function $e^{-iEt/\hbar}$ that depends only on time. For a stationary state, the probability distribution function is independent of time.

A spatial stationary-state wave function $\psi(x)$ for a particle that moves in one dimension in the presence of a potential-energy function $U(x)$ satisfies the time-independent Schrödinger equation. More complex wave functions can be constructed by superposing stationary-state wave functions. These can represent particles that are localized in a certain region, thus representing both particle and wave aspects. (See Examples 40.1 and 40.2.)

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x, t)}{\partial x^2} + U(x)\Psi(x, t)$$

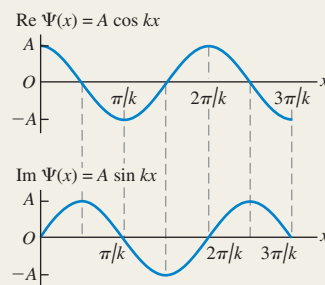$$= i\hbar\frac{\partial\Psi(x, t)}{\partial t} \qquad (40.20)$$

(general 1-D Schrödinger equation)

$$\Psi(x, t) = \psi(x)e^{-iEt/\hbar} \qquad (40.21)$$

(time-dependent wave function for a state of definite energy)

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

(time-independent Schrödinger equation) $\qquad (40.23)$

Re $\Psi(x) = A\cos kx$

Im $\Psi(x) = A\sin kx$

Particle in a box: The energy levels for a particle of mass m in a box (an infinitely deep square potential well) with width L are given by Eq. (40.31). The corresponding normalized stationary-state wave functions of the particle are given by Eq. (40.35). (See Examples 40.3 and 40.4.)

$$E_n = \frac{p_n^2}{2m} = \frac{n^2h^2}{8mL^2} = \frac{n^2\pi^2\hbar^2}{2mL^2}$$

$$(n = 1, 2, 3, \ldots) \qquad (40.31)$$

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}$$

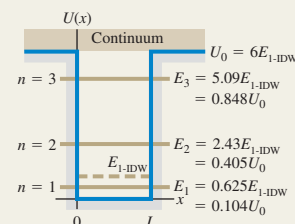$$(n = 1, 2, 3, \ldots) \qquad (40.35)$$
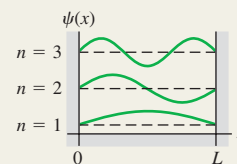
Wave functions and normalization: To be a solution of the Schrödinger equation, the wave function $\psi(x)$ and its derivative $d\psi(x)/dx$ must be continuous everywhere except where the potential-energy function $U(x)$ has an infinite discontinuity. Wave functions are usually normalized so that the total probability of finding the particle somewhere is unity.

$$\int_{-\infty}^{\infty}|\psi(x)|^2\,dx = 1 \qquad (40.33)$$

(normalization condition)
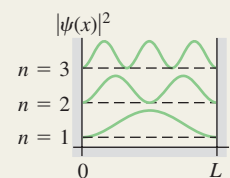
Finite potential well: In a potential well with finite depth U_0, the energy levels are lower than those for an infinitely deep well with the same width, and the number of energy levels corresponding to bound states is finite. The levels are obtained by matching wave functions at the well walls to satisfy the continuity of $\psi(x)$ and $d\psi(x)/dx$. (See Examples 40.5 and 40.6.)

$U(x)$
Continuum
$U_0 = 6E_{1\text{-IDW}}$
$n = 3$ — $E_3 = 5.09E_{1\text{-IDW}}$ $= 0.848U_0$
$n = 2$ — $E_2 = 2.43E_{1\text{-IDW}}$ $= 0.405U_0$
$E_{1\text{-IDW}}$
$n = 1$ — $E_1 = 0.625E_{1\text{-IDW}}$ $= 0.104U_0$

Potential barriers and tunneling: There is a certain probability that a particle will penetrate a potential-energy barrier even though its initial energy is less than the barrier height. This process is called tunneling. (See Example 40.7.)

$U(x)$
U_0
$\psi(x)$

1355
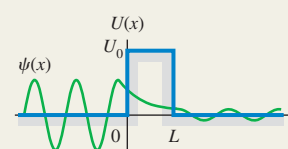
Quantum harmonic oscillator: The energy levels for the harmonic oscillator (for which $U(x) = \frac{1}{2}k'x^2$) are given by Eq. (40.46). The spacing between any two adjacent levels is $\hbar\omega$, where $\omega = \sqrt{k'/m}$ is the oscillation angular frequency of the corresponding Newtonian harmonic oscillator. (See Example 40.8.)

$$E_n = \left(n + \tfrac{1}{2}\right)\hbar\sqrt{\frac{k'}{m}} = \left(n + \tfrac{1}{2}\right)\hbar\omega$$
$$(n = 0, 1, 2, 3, \ldots) \qquad (40.46)$$

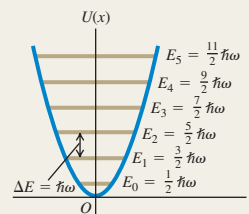

BRIDGING PROBLEM   A Packet in a Box

A particle of mass m in an infinitely deep well has the following wave function in the region from $x = 0$ to $x = L$:

$$\Psi(x, t) = \frac{1}{\sqrt{2}}\psi_1(x)e^{-iE_1 t/\hbar} + \frac{1}{\sqrt{2}}\psi_2(x)e^{-iE_2 t/\hbar}$$

Here $\psi_1(x)$ and $\psi_2(x)$ are the normalized stationary-state wave functions for the first two levels ($n = 1$ and $n = 2$), given by Eq. (40.35). E_1 and E_2, given by Eq. (40.31), are the energies of these levels. The wave function is zero for $x < 0$ and for $x > L$. (a) Find the probability distribution function for this wave function. (b) Does $\Psi(x, t)$ represent a stationary state of definite energy? How can you tell? (c) Show that the wave function $\Psi(x, t)$ is normalized. (d) Find the angular frequency of oscillation of the probability distribution function. What is the interpretation of this oscillation? (e) Suppose instead that $\Psi(x, t)$ is a combination of the wave functions of the two lowest levels of a finite well of length L and height U_0 equal to six times the energy of the lowest-energy bound state of an infinite well of length L. What would be the angular frequency of the probability distribution function in this case?

SOLUTION GUIDE

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IDENTIFY and SET UP

1. In Section 40.1 we saw how to interpret a combination of two free-particle wave functions of different energies. In this problem you need to apply these same ideas to a combination of wave functions for the infinite well (Section 40.2) and the finite well (Section 40.3).

EXECUTE

2. Write down the full time-dependent wave function $\Psi(x, t)$ and its complex conjugate $\Psi^*(x, t)$ using the functions $\psi_1(x)$ and $\psi_2(x)$ from Eq. (40.35). Use these to calculate the probability distribution function, and decide whether or not this function depends on time.

3. To check for normalization, you'll need to verify that when you integrate the probability distribution function from step 2 over all values of x, the integral is equal to 1. [*Hint:* The trigonometric identities $\sin^2\theta = \frac{1}{2}(1 - \cos 2\theta)$ and $\sin\theta\sin\phi = \cos(\theta - \phi) - \cos(\theta + \phi)$ may be helpful.]

4. To find the answer to part (d) you'll need to identify the oscillation angular frequency ω_{osc} in your expression from step 2 for the probability distribution function. To interpret the oscillations, draw graphs of the probability distribution functions at times $t = 0$, $t = T/4$, $t = T/2$, and $t = 3T/4$, where $T = 2\pi/\omega_{osc}$ is the oscillation period of the probability distribution function.

5. For the finite well you do not have simple expressions for the first two stationary-state wave functions $\psi_1(x)$ and $\psi_2(x)$. However, you can still find the oscillation angular frequency ω_{osc}, which is related to the energies E_1 and E_2 in the same way as for the infinite-well case. (Can you see why?)

EVALUATE

6. Why are the factors of $1/\sqrt{2}$ in the wave function $\Psi(x, t)$ important?

7. Why do you suppose the oscillation angular frequency for a finite well is lower than for an infinite well of the same width?

Problems

•, ••, •••: Problems of increasing difficulty. **CP**: Cumulative problems incorporating material from earlier chapters. **CALC**: Problems requiring calculus. **BIO**: Biosciences problems.

DISCUSSION QUESTIONS

Q40.1 If quantum mechanics replaces the language of Newtonian mechanics, why don't we have to use wave functions to describe the motion of macroscopic bodies such as baseballs and cars?

Q40.2 A student remarks that the relationship of ray optics to the more general wave picture is analogous to the relationship of New-tonian mechanics, with well-defined particle trajectories, to quantum mechanics. Comment on this remark.

Q40.3 As Eq. (40.21) indicates, the time-dependent wave function for a stationary state is a complex number having a real part and an imaginary part. How can this function have any physical meaning, since part of it is *imaginary*?

Q40.4 Why must the wave function of a particle be normalized?

Q40.5 If a particle is in a stationary state, does that mean that the particle is not moving? If a particle moves in empty space with constant momentum $\vec{p}$ and hence constant energy $E = p^2/2m$, is it in a stationary state? Explain your answers.

Q40.6 For the particle in a box, we chose $k = n\pi/L$ with $n = 1, 2, 3, \ldots$ to fit the boundary condition that $\psi = 0$ at $x = L$. However, $n = 0, -1, -2, -3, \ldots$ also satisfy that boundary condition. Why didn't we also choose those values of n?

Q40.7 If ψ is normalized, what is the physical significance of the area under a graph of $|\psi|^2$ versus x between x_1 and x_2? What is the total area under the graph of $|\psi|^2$ when all x are included? Explain.

Q40.8 For a particle in a box, what would the probability distribution function $|\psi|^2$ look like if the particle behaved like a classical (Newtonian) particle? Do the actual probability distributions approach this classical form when n is very large? Explain.

Q40.9 In Chapter 15 we represented a standing wave as a superposition of two waves traveling in opposite directions. Can the wave functions for a particle in a box also be thought of as a combination of two traveling waves? Why or why not? What physical interpretation does this representation have? Explain.

Q40.10 A particle in a box is in the ground level. What is the probability of finding the particle in the right half of the box? (Refer to Fig. 40.12, but don't evaluate an integral.) Is the answer the same if the particle is in an excited level? Explain.

Q40.11 The wave functions for a particle in a box (see Fig. 40.12a) are zero at certain points. Does this mean that the particle can't move past one of these points? Explain.

Q40.12 For a particle confined to an infinite square well, is it correct to say that each state of definite energy is also a state of definite wavelength? Is it also a state of definite momentum? Explain. (*Hint:* Remember that momentum is a vector.)

Q40.13 For a particle in a finite potential well, is it correct to say that each bound state of definite energy is also a state of definite wavelength? Is it a state of definite momentum? Explain.

Q40.14 In Fig. 40.12b, the probability function is zero at the points $x = 0$ and $x = L$, the "walls" of the box. Does this mean that the particle never strikes the walls? Explain.

Q40.15 A particle is confined to a finite potential well in the region $0 < x < L$. How does the area under the graph of $|\psi|^2$ in the region $0 < x < L$ compare to the total area under the graph of $|\psi|^2$ when including all possible x?

Q40.16 Compare the wave functions for the first three energy levels for a particle in a box of width L (see Fig. 40.12a) to the corresponding wave functions for a finite potential well of the same width (see Fig. 40.15a). How does the wavelength in the interval $0 \le x \le L$ for the $n = 1$ level of the particle in a box compare to the corresponding wavelength for the $n = 1$ level of the finite potential well? Use this to explain why E_1 is less than $E_{1-\text{IDW}}$ in the situation depicted in Fig. 40.15b.

Q40.17 It is stated in Section 40.3 that a finite potential well always has at least one bound level, no matter how shallow the well. Does this mean that as $U_0 \to 0$, $E_1 \to 0$? Does this violate the Heisenberg uncertainty principle? Explain.

Q40.18 Figure 40.15a shows that the higher the energy of a bound state for a finite potential well, the more the wave function extends outside the well (into the intervals $x < 0$ and $x > L$). Explain why this happens.

Q40.19 In classical (Newtonian) mechanics, the total energy E of a particle can never be less than the potential energy U because the kinetic energy K cannot be negative. Yet in barrier tunneling (see Section 40.4) a particle passes through regions where E is less than U. Is this a contradiction? Explain.

Q40.20 Figure 40.17 shows the scanning tunneling microscope image of 48 iron atoms placed on a copper surface, the pattern indicating the density of electrons on the copper surface. What can you infer about the potential-energy function inside the circle of iron atoms?

Q40.21 Qualitatively, how would you expect the probability for a particle to tunnel through a potential barrier to depend on the height of the barrier? Explain.

Q40.22 The wave function shown in Fig. 40.20 is nonzero for both $x < 0$ and $x > L$. Does this mean that the particle splits into two parts when it strikes the barrier, with one part tunneling through the barrier and the other part bouncing off the barrier? Explain.

Q40.23 The probability distributions for the harmonic oscillator wave functions (see Figs. 40.27 and 40.28) begin to resemble the classical (Newtonian) probability distribution when the quantum number n becomes large. Would the distributions become the same as in the classical case in the limit of very large n? Explain.

Q40.24 In Fig. 40.28, how does the probability of finding a particle in the center half of the region $-A < x < A$ compare to the probability of finding the particle in the outer half of the region? Is this consistent with the physical interpretation of the situation?

Q40.25 Compare the allowed energy levels for the hydrogen atom, the particle in a box, and the harmonic oscillator. What are the values of the quantum number n for the ground level and the second excited level of each system?

Q40.26 Sketch the wave function for the potential-energy well shown in Fig. Q40.26 when E_1 is less than U_0 and when E_3 is greater than U_0.

Figure **Q40.26**
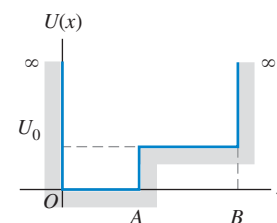
EXERCISES

Section 40.1 Wave Functions and the One-Dimensional Schrödinger Equation

40.1 • An electron is moving as a free particle in the $-x$-direction with momentum that has magnitude 4.50×10^{-24} kg $\cdot$ m/s. What is the one-dimensional time-dependent wave function of the electron?

40.2 • A free particle moving in one dimension has wave function

$$\Psi(x, t) = A\left[e^{i(kx - \omega t)} - e^{i(2kx - 4\omega t)}\right]$$

where k and ω are positive real constants. (a) At $t = 0$ what are the two smallest positive values of x for which the probability function $|\Psi(x, t)|^2$ is a maximum? (b) Repeat part (a) for time $t = 2\pi/\omega$. (c) Calculate v_{av} as the distance the maxima have moved divided by the elapsed time. Compare your result to the expression $v_{av} = (\omega_2 - \omega_1)/(k_2 - k_1)$ from Example 40.1.

40.3 • Consider the free-particle wave function of Example 40.1. Let $k_2 = 3k_1 = 3k$. At $t = 0$ the probability distribution function $|\Psi(x, t)|^2$ has a maximum at $x = 0$. (a) What is the smallest positive value of x for which the probability distribution function has a maximum at time $t = 2\pi/\omega$, where $\omega = \hbar k^2/2m$. (b) From your result in part (a), what is the average speed with which the probability distribution is moving in the $+x$-direction? Compare your result to the expression $v_{av} = (\omega_2 - \omega_1)/(k_2 - k_1)$ from Example 40.1.

40.4 • Consider the free particle of Example 40.1. Show that $v_{av} = (\omega_2 - \omega_1)/(k_2 - k_1)$ can be written as $v_{av} = p_{av}/m$, where $p_{av} = (\hbar k_2 + \hbar k_1)/2$.

40.5 • Consider a wave function given by $\psi(x) = A \sin kx$, where $k = 2\pi/\lambda$ and A is a real constant. (a) For what values of x is there the highest probability of finding the particle described by this wave function? Explain. (b) For which values of x is the probability *zero?* Explain.

40.6 •• Compute $|\Psi|^2$ for $\Psi = \psi \sin \omega t$, where ψ is time independent and ω is a real constant. Is this a wave function for a stationary state? Why or why not?

40.7 • **CALC** Let ψ_1 and ψ_2 be two solutions of Eq. (40.23) with energies E_1 and E_2, respectively, where $E_1 \neq E_2$. Is $\psi = A\psi_1 + B\psi_2$, where A and B are nonzero constants, a solution to Eq. (40.23)? Explain your answer.

40.8 • A particle is described by a wave function $\psi(x) = Ae^{-\alpha x^2}$, where A and α are real, positive constants. If the value of α is increased, what effect does this have on (a) the particle's uncertainty in position and (b) the particle's uncertainty in momentum? Explain your answers.

40.9 • **CALC** **Linear Combinations of Wave Functions.** Let ψ_1 and ψ_2 be two solutions of Eq. (40.23) with the same energy E. Show that $\psi = B\psi_1 + C\psi_2$ is also a solution with energy E, for any values of the constants B and C.

Section 40.2 Particle in a Box

40.10 •• **CALC** A particle moving in one dimension (the x-axis) is described by the wave function

$$\psi(x) = \begin{cases} Ae^{-bx}, & \text{for } x \geq 0 \\ Ae^{bx}, & \text{for } x < 0 \end{cases}$$

where $b = 2.00 \text{ m}^{-1}$, $A > 0$, and the $+x$-axis points toward the right. (a) Determine A so that the wave function is normalized. (b) Sketch the graph of the wave function. (c) Find the probability of finding this particle in each of the following regions: (i) within 50.0 cm of the origin, (ii) on the left side of the origin (can you first guess the answer by looking at the graph of the wave function?), (iii) between $x = 0.500$ m and $x = 1.00$ m.

40.11 • **Ground-Level Billiards.** (a) Find the lowest energy level for a particle in a box if the particle is a billiard ball ($m = 0.20$ kg) and the box has a width of 1.3 m, the size of a billiard table. (Assume that the billiard ball slides without friction rather than rolls; that is, ignore the *rotational* kinetic energy.) (b) Since the energy in part (a) is all kinetic, to what speed does this correspond? How much time would it take at this speed for the ball to move from one side of the table to the other? (c) What is the difference in energy between the $n = 2$ and $n = 1$ levels? (d) Are quantum-mechanical effects important for the game of billiards?

40.12 • A proton is in a box of width L. What must the width of the box be for the ground-level energy to be 5.0 MeV, a typical value for the energy with which the particles in a nucleus are bound? Compare your result to the size of a nucleus—that is, on the order of 10^{-14} m.

40.13 •• Find the width L of a one-dimensional box for which the ground-state energy of an electron in the box equals the absolute value of the ground state of a hydrogen atom.

40.14 •• When a hydrogen atom undergoes a transition from the $n = 2$ to the $n = 1$ level, a photon with $\lambda = 122$ nm is emitted. (a) If the atom is modeled as an electron in a one-dimensional box, what is the width of the box in order for the $n = 2$ to $n = 1$ transition to correspond to emission of a photon of this energy? (b) For a box with the width calculated in part (a), what is the ground-state energy? How does this correspond to the ground-state energy of a hydrogen atom? (c) Do you think a one-dimensional box is a good

model for a hydrogen atom? Explain. (*Hint:* Compare the spacing between adjacent energy levels as a function of n.)

40.15 •• A certain atom requires 3.0 eV of energy to excite an electron from the ground level to the first excited level. Model the atom as an electron in a box and find the width L of the box.

40.16 • An electron in a one-dimensional box has ground-state energy 1.00 eV. What is the wavelength of the photon absorbed when the electron makes a transition to the second excited state?

40.17 • **CALC** Show that the time-dependent wave function given by Eq. (40.35) is a solution to the one-dimensional Schrödinger equation, Eq. (40.23).

40.18 • Recall that $|\psi|^2 \, dx$ is the probability of finding the particle that has normalized wave function $\psi(x)$ in the interval x to $x + dx$. Consider a particle in a box with rigid walls at $x = 0$ and $x = L$. Let the particle be in the ground level and use ψ_n as given in Eq. (40.35). (a) For which values of x, if any, in the range from 0 to L is the probability of finding the particle zero? (b) For which values of x is the probability highest? (c) In parts (a) and (b) are your answers consistent with Fig. 40.12? Explain.

40.19 • Repeat Exercise 40.18 for the particle in the first excited level.

40.20 • **CALC** (a) Show that $\psi = A \sin kx$ is a solution to Eq. (40.25) if $k = \sqrt{2mE}/\hbar$. (b) Explain why this is an acceptable wave function for a particle in a box with rigid walls at $x = 0$ and $x = L$ only if k is an integer multiple of π/L.

40.21 • **CALC** (a) Repeat Exercise 40.20 for $\psi = A \cos kx$. (b) Explain why this cannot be an acceptable wave function for a particle in a box with rigid walls at $x = 0$ and $x = L$ no matter what the value of k.

40.22 • (a) Find the excitation energy from the ground level to the third excited level for an electron confined to a box that has a width of 0.125 nm. (b) The electron makes a transition from the $n = 1$ to $n = 4$ level by absorbing a photon. Calculate the wavelength of this photon.

40.23 • An electron is in a box of width 3.0×10^{-10} m. What are the de Broglie wavelength and the magnitude of the momentum of the electron if it is in (a) the $n = 1$ level; (b) the $n = 2$ level; (c) the $n = 3$ level? In each case how does the wavelength compare to the width of the box?

40.24 •• **CALC** **Normalization of the Wave Function.** Consider a particle moving in one dimension, which we shall call the x-axis. (a) What does it mean for the wave function of this particle to be *normalized*? (b) Is the wave function $\psi(x) = e^{ax}$, where a is a positive real number, normalized? Could this be a valid wave function? (c) If the particle described by the wave function $\psi(x) = Ae^{bx}$, where A and b are positive real numbers, is confined to the range $x \geq 0$, determine A (including its units) so that the wave function is normalized.

Section 40.3 Potential Wells

40.25 • **CALC** (a) Show that $\psi = A \sin kx$, where k is a real (not complex) constant, is *not* a solution of Eq. (40.23) for $U = U_0$ and $E < U_0$. (b) Is this ψ a solution for $E > U_0$?

40.26 •• An electron is moving past the square well shown in Fig. 40.13. The electron has energy $E = 3U_0$. What is the ratio of the de Broglie wavelength of the electron in the region $x > L$ to the wavelength for $0 < x < L$?

40.27 • An electron is bound in a square well of depth $U_0 = 6E_{1-\text{IDW}}$. What is the width of the well if its ground-state energy is 2.00 eV?

40.28 •• An electron is bound in a square well of width 1.50 nm and depth $U_0 = 6E_{1-\text{IDW}}$. If the electron is initially in the ground

level and absorbs a photon, what maximum wavelength can the photon have and still liberate the electron from the well?

40.29 • **CALC** Calculate $d^2\psi/dx^2$ for the wave function of Eq. (40.38), and show that the function is a solution of Eq. (40.37).

40.30 •• An electron is bound in a square well with a depth equal to six times the ground-level energy $E_{1-\text{IDW}}$ of an infinite well of the same width. The longest-wavelength photon that is absorbed by the electron has a wavelength of 400.0 nm. Determine the width of the well.

40.31 •• A proton is bound in a square well of width 4.0 fm = 4.0×10^{-15} m. The depth of the well is six times the ground-level energy $E_{1-\text{IDW}}$ of the corresponding infinite well. If the proton makes a transition from the level with energy E_1 to the level with energy E_3 by absorbing a photon, find the wavelength of the photon.

Section 40.4 Potential Barriers and Tunneling

40.32 •• **Alpha Decay.** In a simple model for a radioactive nucleus, an alpha particle ($m = 6.64 \times 10^{-27}$ kg) is trapped by a square barrier that has width 2.0 fm and height 30.0 MeV. (a) What is the tunneling probability when the alpha particle encounters the barrier if its kinetic energy is 1.0 MeV below the top of the barrier (Fig. E40.32)? (b) What is the tunneling probability if the energy of the alpha particle is 10.0 MeV below the top of the barrier?

Figure **E40.32**
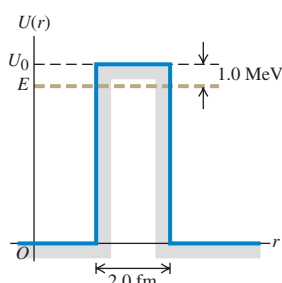
40.33 • An electron with initial kinetic energy 6.0 eV encounters a barrier with height 11.0 eV. What is the probability of tunneling if the width of the barrier is (a) 0.80 nm and (b) 0.40 nm?

40.34 • An electron with initial kinetic energy 5.0 eV encounters a barrier with height U_0 and width 0.60 nm. What is the transmission coefficient if (a) $U_0 = 7.0$ eV; (b) $U_0 = 9.0$ eV; (c) $U_0 = 13.0$ eV?

40.35 •• An electron is moving past the square barrier shown in Fig. 40.19, but the energy of the electron is *greater* than the barrier height. If $E = 2U_0$, what is the ratio of the de Broglie wavelength of the electron in the region $x > L$ to the wavelength for $0 < x < L$?

40.36 • A proton with initial kinetic energy 50.0 eV encounters a barrier of height 70.0 eV. What is the width of the barrier if the probability of tunneling is 3.0×10^{-3}? How does this compare with the barrier width for an electron with the same energy tunneling through a barrier of the same height with the same probability?

40.37 •• (a) An electron with initial kinetic energy 32 eV encounters a square barrier with height 41 eV and width 0.25 nm. What is the probability that the electron will tunnel through the barrier? (b) A proton with the same kinetic energy encounters the same barrier. What is the probability that the proton will tunnel through the barrier?

Section 40.5 The Harmonic Oscillator

40.38 • **CALC** Show that $\psi(x)$ given by Eq. (40.47) is a solution to Eq. (40.44) with energy $E_0 = \hbar\omega/2$.

40.39 • A wooden block with mass 0.250 kg is oscillating on the end of a spring that has force constant 110 N/m. Calculate the ground-level energy and the energy separation between adjacent levels. Express your results in joules and in electron volts. Are quantum effects important?

40.40 • A harmonic oscillator absorbs a photon of wavelength 8.65×10^{-6} m when it undergoes a transition from the ground state to the first excited state. What is the ground-state energy, in electron volts, of the oscillator?

40.41 • Chemists use infrared absorption spectra to identify chemicals in a sample. In one sample, a chemist finds that light of wavelength 5.8 μm is absorbed when a molecule makes a transition from its ground harmonic oscillator level to its first excited level. (a) Find the energy of this transition. (b) If the molecule can be treated as a harmonic oscillator with mass 5.6×10^{-26} kg, find the force constant.

40.42 •• The ground-state energy of a harmonic oscillator is 5.60 eV. If the oscillator undergoes a transition from its $n = 3$ to $n = 2$ level by emitting a photon, what is the wavelength of the photon?

40.43 • In Section 40.5 it is shown that for the ground level of a harmonic oscillator, $\Delta x \Delta p_x = \hbar/2$. Do a similar analysis for an excited level that has quantum number n. How does the uncertainty product $\Delta x \Delta p_x$ depend on n?

40.44 •• For the ground-level harmonic oscillator wave function $\psi(x)$ given in Eq. (40.47), $|\psi|^2$ has a maximum at $x = 0$. (a) Compute the ratio of $|\psi|^2$ at $x = +A$ to $|\psi|^2$ at $x = 0$, where A is given by Eq. (40.48) with $n = 0$ for the ground level. (b) Compute the ratio of $|\psi|^2$ at $x = +2A$ to $|\psi|^2$ at $x = 0$. In each case is your result consistent with what is shown in Fig. 40.27?

40.45 •• For the sodium atom of Example 40.8, find (a) the ground-state energy, (b) the wavelength of a photon emitted when the $n = 4$ to $n = 3$ transition occurs; (c) the energy difference for any $\Delta n = 1$ transition.

PROBLEMS

40.46 • The discussion in Section 40.1 shows that the wave function $\Psi = \psi e^{-i\omega t}$ is a stationary state, where ψ is time independent and ω is a real (not complex) constant. Consider the wave function $\Psi = \psi_1 e^{-i\omega_1 t} + \psi_2 e^{-i\omega_2 t}$, where ψ_1 and ψ_2 are different time-independent functions and ω_1 and ω_2 are different real constants. Assume that ψ_1 and ψ_2 are real-valued functions, so that $\psi_1^* = \psi_1$ and $\psi_2^* = \psi_2$. Is this Ψ a wave function for a stationary state? Why or why not?

40.47 •• A particle of mass m in a one-dimensional box has the following wave function in the region $x = 0$ to $x = L$:

$$\Psi(x, t) = \frac{1}{\sqrt{2}}\psi_1(x)e^{-iE_1 t/\hbar} + \frac{1}{\sqrt{2}}\psi_3(x)e^{-iE_3 t/\hbar}$$

Here $\psi_1(x)$ and $\psi_3(x)$ are the normalized stationary-state wave functions for the $n = 1$ and $n = 3$ levels, and E_1 and E_3 are the energies of these levels. The wave function is zero for $x < 0$ and for $x > L$. (a) Find the value of the probability distribution function at $x = L/2$ as a function of time. (b) Find the angular frequency at which the probability distribution function oscillates.

40.48 •• **CALC** Consider the wave packet defined by

$$\psi(x) = \int_0^\infty B(k)\cos kx\, dk$$

Let $B(k) = e^{-\alpha^2 k^2}$. (a) The function $B(k)$ has its maximum value at $k = 0$. Let k_h be the value of k at which $B(k)$ has fallen to half its maximum value, and define the width of $B(k)$ as $w_k = k_h$. In terms of α, what is w_k? (b) Use integral tables to evaluate the integral that gives $\psi(x)$. For what value of x is $\psi(x)$ maximum? (c) Define the width of $\psi(x)$ as $w_x = x_h$, where x_h is the positive

value of x at which $\psi(x)$ has fallen to half its maximum value. Calculate w_x in terms of α. (d) The momentum p is equal to $hk/2\pi$, so the width of B in momentum is $w_p = hw_k/2\pi$. Calculate the product $w_p w_x$ and compare to the Heisenberg uncertainty principle.

40.49 •• **CALC** (a) Using the integral in Problem 40.48, determine the wave function $\psi(x)$ for a function $B(k)$ given by

$$B(k) = \begin{cases} 0 & k < 0 \\ 1/k_0, & 0 \le k \le k_0 \\ 0, & k > k_0 \end{cases}$$

This represents an equal combination of all wave numbers between 0 and k_0. Thus $\psi(x)$ represents a particle with average wave number $k_0/2$, with a total spread or uncertainty in wave number of k_0. We will call this spread the *width* w_k of $B(k)$, so $w_k = k_0$. (b) Graph $B(k)$ versus k and $\psi(x)$ versus x for the case $k_0 = 2\pi/L$, where L is a length. Locate the point where $\psi(x)$ has its maximum value and label this point on your graph. Locate the two points closest to this maximum (one on each side of it) where $\psi(x) = 0$, and define the distance along the x-axis between these two points as w_x, the width of $\psi(x)$. Indicate the distance w_x on your graph. What is the value of w_x if $k_0 = 2\pi/L$? (c) Repeat part (b) for the case $k_0 = \pi/L$. (d) The momentum p is equal to $hk/2\pi$, so the width of B in momentum is $w_p = hw_k/2\pi$. Calculate the product $w_p w_x$ for each of the cases $k_0 = 2\pi/L$ and $k_0 = \pi/L$. Discuss your results in light of the Heisenberg uncertainty principle.

40.50 • **CALC** Show that the wave function $\psi(x) = Ae^{ikx}$ is a solution of Eq. (40.23) for a particle of mass m, in a region where the potential energy is a constant $U_0 < E$. Find an expression for k, and relate it to the particle's momentum and to its de Broglie wavelength.

40.51 •• **CALC** Wave functions like the one in Problem 40.50 can represent free particles moving with velocity $v = p/m$ in the x-direction. Consider a beam of such particles incident on a potential-energy step $U(x) = 0$, for $x < 0$, and $U(x) = U_0 < E$, for $x > 0$. The wave function for $x < 0$ is $\psi(x) = Ae^{ik_1x} + Be^{-ik_1x}$, representing incident and reflected particles, and for $x > 0$ is $\psi(x) = Ce^{ik_2x}$, representing transmitted particles. Use the conditions that both ψ and its first derivative must be continuous at $x = 0$ to find the constants B and C in terms of k_1, k_2, and A.

40.52 • Let ΔE_n be the energy difference between the adjacent energy levels E_n and E_{n+1} for a particle in a box. The ratio $R_n = \Delta E_n/E_n$ compares the energy of a level to the energy separation of the next higher energy level. (a) For what value of n is R_n largest, and what is this largest R_n? (b) What does R_n approach as n becomes very large? How does this result compare to the classical value for this quantity?

40.53 • **Photon in a Dye Laser.**   An electron in a long, organic molecule used in a dye laser behaves approximately like a particle in a box with width 4.18 nm. What is the wavelength of the photon emitted when the electron undergoes a transition (a) from the first excited level to the ground level and (b) from the second excited level to the first excited level?

40.54 • **CALC** A particle is in the ground level of a box that extends from $x = 0$ to $x = L$. (a) What is the probability of finding the particle in the region between 0 and $L/4$? Calculate this by integrating $|\psi(x)|^2\,dx$, where ψ is normalized, from $x = 0$ to $x = L/4$. (b) What is the probability of finding the particle in the region $x = L/4$ to $x = L/2$? (c) How do the results of parts (a) and (b) compare? Explain. (d) Add the probabilities calculated in parts (a) and (b). (e) Are your results in parts (a), (b), and (d) consistent with Fig. 40.12b? Explain.

40.55 •• **CALC** What is the probability of finding a particle in a box of length L in the region between $x = L/4$ and $x = 3L/4$ when the particle is in (a) the ground level and (b) the first excited level? (*Hint:* Integrate $|\psi(x)|^2\,dx$, where ψ is normalized, between $L/4$ and $3L/4$.) (c) Are your results in parts (a) and (b) consistent with Fig. 40.12b? Explain.

40.56 •• Consider a particle in a box with rigid walls at $x = 0$ and $x = L$. Let the particle be in the ground level. Calculate the probability $|\psi|^2\,dx$ that the particle will be found in the interval x to $x + dx$ for (a) $x = L/4$; (b) $x = L/2$; (c) $x = 3L/4$.

40.57 •• Repeat Problem 40.56 for a particle in the first excited level.

40.58 •• **CP** A particle is confined within a box with perfectly rigid walls at $x = 0$ and $x = L$. Although the magnitude of the instantaneous force exerted on the particle by the walls is infinite and the time over which it acts is zero, the impulse (that involves a product of force and time) is both finite and quantized. Show that the impulse exerted by the wall at $x = 0$ is $(nh/L)\hat{\imath}$ and that the impulse exerted by the wall at $x = L$ is $-(nh/L)\hat{\imath}$. (*Hint:* You may wish to review Section 8.1.)

40.59 •• **CALC** A fellow student proposes that a possible wave function for a free particle with mass m (one for which the potential-energy function $U(x)$ is zero) is

$$\psi(x) = \begin{cases} e^{+\kappa x}, & x < 0 \\ e^{-\kappa x}, & x \ge 0 \end{cases}$$

where κ is a positive constant. (a) Graph this proposed wave function. (b) Show that the proposed wave function satisfies the Schrödinger equation for $x < 0$ if the energy is $E = -\hbar^2\kappa^2/2m$—that is, if the energy of the particle is *negative*. (c) Show that the proposed wave function also satisfies the Schrödinger equation for $x \ge 0$ with the same energy as in part (b). (d) Explain why the proposed wave function is nonetheless *not* an acceptable solution of the Schrödinger equation for a free particle. (*Hint:* What is the behavior of the function at $x = 0$?) It is in fact impossible for a free particle (one for which $U(x) = 0$) to have an energy less than zero.

40.60 •• The *penetration distance* η in a finite potential well is the distance at which the wave function has decreased to $1/e$ of the wave function at the classical turning point:

$$\psi(x = L + \eta) = \frac{1}{e}\psi(L)$$

The penetration distance can be shown to be

$$\eta = \frac{\hbar}{\sqrt{2m(U_0 - E)}}$$

The probability of finding the particle beyond the penetration distance is nearly zero. (a) Find η for an electron having a kinetic energy of 13 eV in a potential well with $U_0 = 20$ eV. (b) Find η for a 20.0-MeV proton trapped in a 30.0-MeV-deep potential well.

40.61 • **CALC** (a) For the finite potential well of Fig. 40.13, what relationships among the constants A and B of Eq. (40.38) and C and D of Eq. (40.40) are obtained by applying the boundary condition that ψ be continuous at $x = 0$ and at $x = L$? (b) What relationships among A, B, C, and D are obtained by applying the boundary condition that $d\psi/dx$ be continuous at $x = 0$ and at $x = L$?

40.62 • An electron with initial kinetic energy 5.5 eV encounters a square potential barrier with height 10.0 eV. What is the width of

the barrier if the electron has a 0.10% probability of tunneling through the barrier?

40.63 •• A particle with mass m and total energy E tunnels through a square barrier of height U_0 and width L. When the transmission coefficient is *not* much less than unity, it is given by

$$T = \left[1 + \frac{(U_0 \sinh \kappa L)^2}{4E(U_0 - E)}\right]^{-1}$$

where $\sinh \kappa L = (e^{\kappa L} - e^{-\kappa L})/2$ is the hyperbolic sine of κL. (a) Show that if $\kappa L \gg 1$, this expression for T approaches Eq. (40.42). (b) Explain why the restriction $\kappa L \gg 1$ in part (a) implies either that the barrier is relatively wide or that the energy E is relatively low compared to U_0. (c) Show that as the particle's incident kinetic energy E approaches the barrier height U_0, T approaches $[1 + (kL/2)^2]^{-1}$, where $k = \sqrt{2mE}/\hbar$ is the wave number of the incident particle. (*Hint:* If $|z| \ll 1$, then $\sinh z \approx z$.)

40.64 • **CP** A harmonic oscillator consists of a 0.020-kg mass on a spring. Its frequency is 1.50 Hz, and the mass has a speed of 0.360 m/s as it passes the equilibrium position. (a) What is the value of the quantum number n for its energy level? (b) What is the difference in energy between the levels E_n and E_{n+1}? Is this difference detectable?

40.65 • For small amplitudes of oscillation the motion of a pendulum is simple harmonic. For a pendulum with a period of 0.500 s, find the ground-level energy and the energy difference between adjacent energy levels. Express your results in joules and in electron volts. Are these values detectable?

40.66 •• Some 164.9-nm photons are emitted in a $\Delta n = 1$ transition within a solid-state lattice. The lattice is modeled as electrons in a box having length 0.500 nm. What transition corresponds to the emitted light?

40.67 •• **CALC** Show that for $\psi(x)$ given by Eq. (40.47), the probability distribution function has a maximum at $x = 0$.

40.68 •• **CALC** (a) Show by direct substitution in the Schrödinger equation for the one-dimensional harmonic oscillator that the wave function $\psi_1(x) = A_1 x e^{-\alpha^2 x^2/2}$, where $\alpha^2 = m\omega/\hbar$, is a solution with energy corresponding to $n = 1$ in Eq. (40.46). (b) Find the normalization constant A_1. (c) Show that the probability density has a minimum at $x = 0$ and maxima at $x = \pm 1/\alpha$, corresponding to the classical turning points for the ground state $n = 0$.

40.69 •• **CP** (a) The wave nature of particles results in the quantum-mechanical situation that a particle confined in a box can assume only wavelengths that result in standing waves in the box, with nodes at the box walls. Use this to show that an electron confined in a one-dimensional box of length L will have energy levels given by

$$E_n = \frac{n^2 h^2}{8mL^2}$$

(*Hint:* Recall that the relationship between the de Broglie wavelength and the speed of a nonrelativistic particle is $mv = h/\lambda$. The energy of the particle is $\frac{1}{2}mv^2$.) (b) If a hydrogen atom is modeled as a one-dimensional box with length equal to the Bohr radius, what is the energy (in electron volts) of the lowest energy level of the electron?

40.70 ••• Consider a potential well defined as $U(x) = \infty$ for $x < 0$, $U(x) = 0$ for $0 < x < L$, and $U(x) = U_0 > 0$ for $x > L$ (Fig. P40.70). Consider a particle with mass m and kinetic energy $E < U_0$ that is trapped in the well. (a) The boundary condition at the infinite wall $(x = 0)$ is $\psi(0) = 0$. What must the form of

the function $\psi(x)$ for $0 < x < L$ be in order to satisfy both the Schrödinger equation and this boundary condition? (b) The wave function must remain finite as $x \rightarrow \infty$. What must the form of the function $\psi(x)$ for $x > L$ be in order to satisfy both the Schrödinger equation and this boundary condition at infinity? (c) Impose the boundary conditions that ψ and $d\psi/dx$ are continuous at $x = L$. Show that the energies of the allowed levels are obtained from solutions of the equation $k \cot kL = -\kappa$, where $k = \sqrt{2mE}/\hbar$ and $\kappa = \sqrt{2m(U_0 - E)}/\hbar$.

Figure **P40.70**

40.71 ••• Section 40.2 considered a box with walls at $x = 0$ and $x = L$. Now consider a box with width L but centered at $x = 0$, so that it extends from $x = -L/2$ to $x = +L/2$ (Fig. P40.71). Note that this box is symmetric about $x = 0$. (a) Consider possible wave functions of the form $\psi(x) = A \sin kx$. Apply the boundary conditions at the wall to obtain the allowed energy levels. (b) Another set of possible wave functions are functions of the form $\psi(x) = A \cos kx$. Apply the boundary conditions at the wall to obtain the allowed energy levels. (c) Compare the energies obtained in parts (a) and (b) to the set of energies given in Eq. (40.31). (d) An odd function f satisfies the condition $f(x) = -f(-x)$, and an even function g satisfies $g(x) = g(-x)$. Of the wave functions from parts (a) and (b), which are even and which are odd?
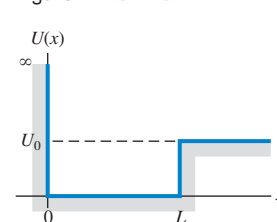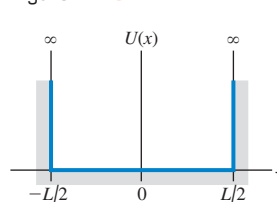
Figure **P40.71**

CHALLENGE PROBLEMS

40.72 ••• **CALC** **The WKB Approximation.** It can be a challenge to solve the Schrödinger equation for the bound-state energy levels of an arbitrary potential well. An alternative approach that can yield good approximate results for the energy levels is the *WKB approximation* (named for the physicists Gregor Wentzel, Hendrik Kramers, and Léon Brillouin, who pioneered its application to quantum mechanics). The WKB approximation begins from three physical statements: (i) According to de Broglie, the magnitude of momentum p of a quantum-mechanical particle is $p = h/\lambda$. (ii) The magnitude of momentum is related to the kinetic energy K by the relationship $K = p^2/2m$. (iii) If there are no nonconservative forces, then in Newtonian mechanics the energy E for a particle is constant and equal at each point to the sum of the kinetic and potential energies at that point: $E = K + U(x)$, where x is the coordinate. (a) Combine these three relationships to show that the wavelength of the particle at a coordinate x can be written as

$$\lambda(x) = \frac{h}{\sqrt{2m[E - U(x)]}}$$

Thus we envision a quantum-mechanical particle in a potential well $U(x)$ as being like a free particle, but with a wavelength $\lambda(x)$ that is a function of position. (b) When the particle moves into a region of increasing potential energy, what happens to its wavelength? (c) At a point where $E = U(x)$, Newtonian mechanics says that the particle has zero kinetic energy and must be instantaneously at rest. Such a point is called a *classical turning point,* since this is where a Newtonian particle must stop its motion and

reverse direction. As an example, an object oscillating in simple harmonic motion with amplitude A moves back and forth between the points $x = -A$ and $x = +A$; each of these is a classical turning point, since there the potential energy $\frac{1}{2}k'x^2$ equals the total energy $\frac{1}{2}k'A^2$. In the WKB expression for $\lambda(x)$, what is the wavelength at a classical turning point? (d) For a particle in a box with length L, the walls of the box are classical turning points (see Fig. 40.8). Furthermore, the number of wavelengths that fit within the box must be a half-integer (see Fig. 40.10), so that $L = (n/2)\lambda$ and hence $L/\lambda = n/2$, where $n = 1, 2, 3, \ldots$. [Note that this is a restatement of Eq. (40.29).] The WKB scheme for finding the allowed bound-state energy levels of an *arbitrary* potential well is an extension of these observations. It demands that for an allowed energy E, there must be a half-integer number of wavelengths between the classical turning points for that energy. Since the wavelength in the WKB approximation is not a constant but depends on x, the number of wavelengths between the classical turning points a and b for a given value of the energy is the integral of $1/\lambda(x)$ between those points:

$$\int_a^b \frac{dx}{\lambda(x)} = \frac{n}{2} \quad (n = 1, 2, 3, \ldots)$$

Using the expression for $\lambda(x)$ you found in part (a), show that the *WKB condition for an allowed bound-state energy* can be written as

$$\int_a^b \sqrt{2m[E - U(x)]} \, dx = \frac{nh}{2} \quad (n = 1, 2, 3, \ldots)$$

(e) As a check on the expression in part (d), apply it to a particle in a box with walls at $x = 0$ and $x = L$. Evaluate the integral and show that the allowed energy levels according to the WKB approximation are the same as those given by Eq. (40.31). (*Hint:* Since the walls of the box are infinitely high, the points $x = 0$ and $x = L$ are classical turning points for *any* energy E. Inside the box, the potential energy is zero.) (f) For the finite square well shown in Fig. 40.13, show that the WKB expression given in part (d) predicts the *same* bound-state energies as for an infinite square well of the same width. (*Hint:* Assume $E < U_0$. Then the classical turning points are at $x = 0$ and $x = L$.) This shows that the WKB approximation does a poor job when the potential-energy function changes discontinuously, as for a finite potential well. In the next two problems we consider situations in which the potential-energy function changes gradually and the WKB approximation is much more useful.
40.73 ••• **CALC** The WKB approximation (see Challenge Problem 40.72) can be used to calculate the energy levels for a harmonic oscillator. In this approximation, the energy levels are the solutions to the equation

$$\int_a^b \sqrt{2m[E - U(x)]} \, dx = \frac{nh}{2} \quad n = 1, 2, 3, \ldots$$

Here E is the energy, $U(x)$ is the potential-energy function, and $x = a$ and $x = b$ are the classical turning points (the points at

which E is equal to the potential energy, so the Newtonian kinetic energy would be zero). (a) Determine the classical turning points for a harmonic oscillator with energy E and force constant k'. (b) Carry out the integral in the WKB approximation and show that the energy levels in this approximation are $E_n = \hbar\omega$, where $\omega = \sqrt{k'/m}$ and $n = 1, 2, 3, \ldots$. (*Hint:* Recall that $\hbar = h/2\pi$. A useful standard integral is

$$\int \sqrt{A^2 - x^2} \, dx = \frac{1}{2}\left[x\sqrt{A^2 - x^2} + A^2 \arcsin\left(\frac{x}{|A|}\right) \right]$$

where arcsin denotes the inverse sine function. Note that the integrand is even, so the integral from $-x$ to x is equal to twice the integral from 0 to x.) (c) How do the approximate energy levels found in part (b) compare with the true energy levels given by Eq. (40.46)? Does the WKB approximation give an underestimate or an overestimate of the energy levels?
40.74 ••• **CALC** Protons, neutrons, and many other particles are made of more fundamental particles called *quarks* and *antiquarks* (the antimatter equivalent of quarks). A quark and an antiquark can form a bound state with a variety of different energy levels, each of which corresponds to a different particle observed in the laboratory. As an example, the ψ particle is a low-energy bound state of a so-called charm quark and its antiquark, with a rest energy of 3097 MeV; the $\psi(2S)$ particle is an excited state of this same quark–antiquark combination, with a rest energy of 3686 MeV. A simplified representation of the potential energy of interaction between a quark and an antiquark is $U(x) = A|x|$, where A is a positive constant and x represents the distance between the quark and the antiquark. You can use the WKB approximation (see Challenge Problem 40.72) to determine the bound-state energy levels for this potential-energy function. In the WKB approximation, the energy levels are the solutions to the equation

$$\int_a^b \sqrt{2m[E - U(x)]} \, dx = \frac{nh}{2} \quad (n = 1, 2, 3, \ldots)$$

Here E is the energy, $U(x)$ is the potential-energy function, and $x = a$ and $x = b$ are the classical turning points (the points at which E is equal to the potential energy, so the Newtonian kinetic energy would be zero). (a) Determine the classical turning points for the potential $U(x) = A|x|$ and for an energy E. (b) Carry out the above integral and show that the allowed energy levels in the WKB approximation are given by

$$E_n = \frac{1}{2m}\left(\frac{3mAh}{4}\right)^{2/3} n^{2/3} \quad (n = 1, 2, 3, \ldots)$$

(*Hint:* The integrand is even, so the integral from $-x$ to x is equal to twice the integral from 0 to x.) (c) Does the difference in energy between successive levels increase, decrease, or remain the same as n increases? How does this compare to the behavior of the energy levels for the harmonic oscillator? For the particle in a box? Can you suggest a simple rule that relates the difference in energy between successive levels to the shape of the potential-energy function?

Answers

Chapter Opening Question ?

When an electron in one of these particles—called *quantum dots*—makes a transition from an excited level to a lower level, it emits a photon whose energy is equal to the difference in energy between the levels. The smaller the quantum dot, the larger the energy spacing between levels and hence the shorter (bluer) the wavelength of the emitted photons. See Example 40.6 (Section 40.3) for more details.

Test Your Understanding Questions

40.1 Answer: no Equation (40.19) represents a superposition of wave functions with different values of wave number k and hence different values of energy $E = \hbar^2 k^2 / 2m$. The state that this combined wave function represents is not a state of definite energy, and therefore not a stationary state. Another way to see this is to note that there is a factor $e^{-iEt/\hbar}$ inside the integral in Eq. (40.19), with a different value of E for each value of k. This wave function therefore has a very complicated time dependence, and the probability distribution function $|\Psi(x, t)|^2$ does depend on time.

40.2 Answer: (v) Our derivation of the stationary-state wave functions for a particle in a box shows that they are superpositions of waves propagating in opposite directions, just like a standing wave on a string. One wave has momentum in the positive x-direction, while the other wave has an equal magnitude of momentum in the negative x-direction. The *total* x-component of momentum is zero.

40.3 Answer: (i) The energy levels are arranged as shown in Fig. 40.15b if $U_0 = 6E_{1-\text{IDW}}$, where $E_{1-\text{IDW}} = \pi^2 \hbar^2 / 2mL^2$ is the ground-level energy of an infinite well. If the well width L is reduced to one-half of its initial value, $E_{1-\text{IDW}}$ increases by a factor of four and so U_0 must also increase by a factor of four. The energies E_1, E_2, and E_3 shown in Fig. 40.15b are all specific fractions of U_0, so they will also increase by a factor of four.

40.4 Answer: yes Figure 40.20 shows a possible wave function $\psi(x)$ for tunneling. Since $\psi(x)$ is not zero within the barrier $(0 \le x \le L)$, there is some probability that the particle can be found there.

40.5 Answer: (ii) If the second photon has a longer wavelength and hence lower energy than the first photon, the difference in energy between the first and second excited levels must be less than the difference between the ground level and the first excited level. This is the case for the hydrogen atom, for which the energy difference between levels decreases as the energy increases (see Fig. 39.24). By contrast, the energy difference between successive levels increases for a particle in a box (see Fig. 40.11b) and is constant for a harmonic oscillator (see Fig. 40.25).

Bridging Problem

Answers: (a)

$$|\Psi(x, t)|^2 = \frac{1}{L}\left[\sin^2\frac{\pi x}{L} + \sin^2\frac{2\pi x}{L} \right.$$
$$\left. + 2\sin\frac{\pi x}{L}\sin\frac{2\pi x}{L}\cos\left(\frac{(E_2 - E_1)t}{\hbar}\right) \right]$$

(b) no   **(c)** yes   **(d)** $\dfrac{3\pi^2\hbar}{2mL^2}$ **(e)** $\dfrac{0.905\pi^2\hbar}{mL^2}$