6

Quantum Mechanics in One Dimension

Chapter Outline

We have seen that associated with any particle is a matter wave called the **wavefunction.** How this wavefunction affects our description of a particle and its behavior is the subject of **quantum mechanics,** or wave mechanics. This scheme, developed from 1925 to 1926 by Schrödinger, Heisenberg, and others, makes it possible to understand a host of phenomena involving elementary particles, atoms, molecules, and solids. In this and subsequent chapters, we shall describe the basic features of wave mechanics and its application to simple systems. The relevant concepts for particles confined to motion along a straight line (the *x*-axis) are developed in the present chapter.

6.1 THE BORN INTERPRETATION

The wavefunction Ψ contains within it all the information that can be known about the particle. That basic premise forms the cornerstone of our investigation: One of our objectives will be to discover how information may be extracted from the wavefunction; the other, to learn how to obtain this wavefunction for a given system.

The currently held view connects the wavefunction Ψ with *probabilities* in the manner first proposed by Max Born in 1925:

191

Max Born was a German theoretical physicist who made major contributions in many areas of physics, including relativity, atomic and solid-state physics, matrix mechanics, the quantum mechanical treatment of particle scattering ("Born approximation"), the foundations of quantum mechanics (Born interpretation of Ψ), optics, and the kinetic theory of liquids. Born received the doctorate in physics from the University of Göttingen in 1907, and he acquired an extensive knowledge of mathematics as the private assistant to the great German mathematician David Hilbert. This strong mathematical background proved a great asset when he was quickly able to reformulate Heisenberg's quantum theory in a more consistent way with matrices.

In 1921, Born was offered a post at the University of Göttingen, where he helped build one of the strongest physics centers of the 20th century. This group consisted, at one time or another, of the mathematicians Hilbert, Courant, Klein, and Runge and the physicists Born, Jordan, Heisenberg, Franck, Pohl, Heitler, Herzberg, Nordheim, and Wigner,

Image not available due to copyright restrictions

MAX BORN

(1882–1970)

among others. In 1926, shortly after Schrödinger's publication of wave mechanics, Born applied Schrödinger's methods to atomic scattering and developed the Born approximation method for carrying out calculations of the probability of scattering of a particle into a given solid angle. This work furnished the basis for Born's startling (in 1926) interpretation of $|\Psi|^2$ as the probability density. For this so-called statistical interpretation of $|\Psi|^2$ he was awarded the Nobel prize in 1954.

Fired by the Nazis, Born left Germany in 1933 for Cambridge and eventually the University of Edinburgh, where he again became the leader of a large group investigating the statistical mechanics of condensed matter. In his later years, Born campaigned against atomic weapons, wrote an autobiography, and translated German humorists into English.

Born interpretation of Ψ

The probability that a particle will be found in the infinitesimal interval dx about the point x, denoted by $P(x)\,dx$, is

$$P(x)\,dx = |\Psi(x,t)|^2\,dx \tag{6.1}$$

Therefore, although it is not possible to specify with certainty the location of a particle, it is possible to assign probabilities for observing it at any given position. The quantity $|\Psi|^2$, the square of the absolute value of Ψ, represents the intensity of the matter wave and is computed as the product of Ψ with its complex conjugate, that is, $|\Psi|^2 = \Psi^*\Psi$. Notice that Ψ itself is not a measurable quantity; however, $|\Psi|^2$ is measurable and is just the probability per unit length, or **probability density** $P(x)$, for finding the particle at the point x at time t. For example, the intensity distribution in a light diffraction pattern is a measure of the probability that a photon will strike a given point within the pattern. Because of its relation to probabilities, we insist that $\Psi(x, t)$ be a *single-valued and continuous function of x* and t so that no ambiguities can arise concerning the predictions of the theory. The wavefunction Ψ also should be *smooth*, a condition that will be elaborated later as it is needed.

Because the particle must be somewhere along the x-axis, the probabilities summed over all values of x must add to 1:

$$\int_{-\infty}^{\infty} |\Psi(x, t)|^2\, dx = 1 \qquad (6.2)$$

Any wavefunction satisfying Equation 6.2 is said to be **normalized.** Normalization is simply a statement that the particle can be found somewhere with certainty. The probability of finding the particle in any finite interval $a \leq x \leq b$ is

$$P = \int_{a}^{b} |\Psi(x, t)|^2\, dx \qquad (6.3)$$

That is, the probability is just the area included under the curve of probability density between the points $x = a$ and $x = b$ (Fig. 6.1).
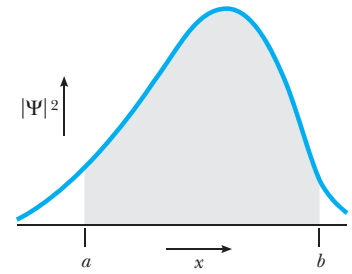

Figure 6.1 The probability for a particle to be in the interval $a \leq x \leq b$ is the area under the curve from a to b of the probability density function $|\Psi(x, t)|^2$.

EXAMPLE 6.1   Normalizing the Wavefunction

The initial wavefunction of a particle is given as $\Psi(x, 0) = C\exp(-|x|/x_0)$, where C and x_0 are constants. Sketch this function. Find C in terms of x_0 such that $\Psi(x, 0)$ is normalized.

Solution The given wavefunction is symmetric, decaying exponentially from the origin in either direction, as shown in Figure 6.2. The decay length x_0 represents the
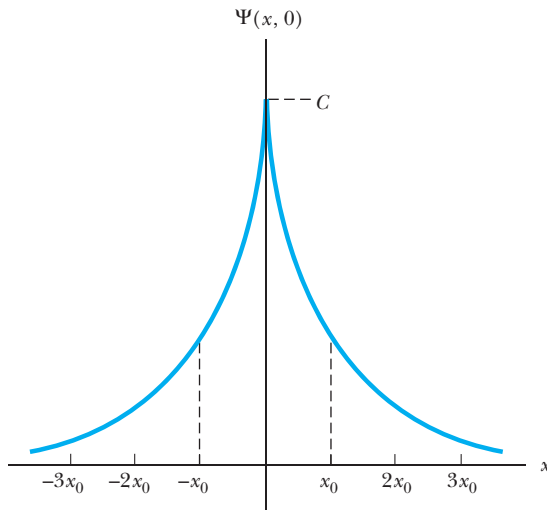

Figure 6.2   (Example 6.1) The symmetric wavefunction $\Psi(x, 0) = C\exp(-|x|/x_0)$. At $x = \pm x_0$ the wave amplitude is down by the factor $1/e$ from its peak value $\Psi(0, 0) = C$. C is a normalizing constant whose proper value is $C = 1/\sqrt{x_0}$.

distance over which the wave amplitude is diminished by the factor $1/e$ from its maximum value $\Psi(0, 0) = C$.

The normalization requirement is

$$1 = \int_{-\infty}^{\infty} |\Psi(x, 0)|^2\, dx = C^2 \int_{-\infty}^{\infty} e^{-2|x|/x_0}\, dx$$

Because the integrand is unchanged when x changes sign (it is an even function), we may evaluate the integral over the whole axis as twice that over the half-axis $x > 0$, where $|x| = x$. Then,

$$1 = 2C^2 \int_{0}^{\infty} e^{-2x/x_0}\, dx = 2C^2\left(\frac{x_0}{2}\right) = C^2 x_0$$

Thus, we must take $C = 1/\sqrt{x_0}$ for normalization.

EXAMPLE 6.2   Calculating Probabilities

Calculate the probability that the particle in the preceding example will be found in the interval $-x_0 \leq x \leq x_0$.

Solution   The probability is the area under the curve of $|\Psi(x, 0)|^2$ from $-x_0$ to $+x_0$ and is obtained by integrating the probability density over the specified interval:

$$P = \int_{-x_0}^{x_0} |\Psi(x, 0)|^2\, dx = 2\int_{0}^{x_0} |\Psi(x, 0)|^2\, dx$$

where the second step follows because the integrand is an even function, as discussed in Example 6.1. Thus,

$$P = 2C^2 \int_{0}^{x_0} e^{-2x/x_0}\, dx = 2C^2(x_0/2)(1 - e^{-2})$$

Substituting $C = 1/\sqrt{x_0}$ into this expression gives for the probability $P = 1 - e^{-2} = 0.8647$, or about 86.5%, independent of x_0.

The fundamental problem of quantum mechanics is this: Given the wavefunction at some initial instant, say $t = 0$, find the wavefunction at any subsequent time t. The wavefunction $\Psi(x, 0)$ represents the initial information that must be specified; once this is known, however, the wave propagates according to prescribed laws of nature.

Because it describes how a given system evolves, quantum mechanics is a dynamical theory much like Newtonian mechanics. There are, of course, important differences. In Newton's mechanics, the state of a particle at $t = 0$ is specified by giving its initial position $x(0)$ and velocity $v(0)$—just two numbers; quantum mechanics demands an entire wavefunction $\Psi(x, 0)$—an infinite set of numbers corresponding to the wavefunction value at every point x. But both theories describe how this state changes with time when the forces acting on the particle are known. In Newton's mechanics $x(t)$ and $v(t)$ are calculated from Newton's second law; in quantum mechanics $\Psi(x, t)$ must be calculated from another law—*Schrödinger's equation.*

6.2   WAVEFUNCTION FOR A FREE PARTICLE

A free particle is one subject to no force. This special case can be studied using prior assumptions without recourse to the Schrödinger equation. The development underscores the role of the initial conditions in quantum physics.

The wavenumber k and frequency ω of free particle matter waves are given by the de Broglie relations

$$k = \frac{p}{\hbar} \quad \text{and} \quad \omega = \frac{E}{\hbar} \tag{6.4}$$

For nonrelativistic particles ω is related to k as

$$\omega(k) = \frac{\hbar k^2}{2m} \tag{6.5}$$

which follows from the classical connection $E = p^2/2m$ between the energy E and momentum p for a free particle.[1]

For the wavefunction itself, we should take

Plane wave representation for a free particle

$$\Psi_k(x, t) = Ae^{i(kx - \omega t)} = A\{\cos(kx - \omega t) + i\sin(kx - \omega t)\} \tag{6.6}$$

where $i = \sqrt{-1}$ is the imaginary unit. This is an oscillation with wavenumber k, frequency ω, and amplitude A. Because the variables x and t occur only in the combination $kx - \omega t$, the oscillation is a traveling wave, as befits a free particle in motion. Further, the particular combination expressed by Equation 6.6 is that of a plane wave,[2] for which the probability density $|\Psi|^2 (= A^2)$ is *uniform.* That is, the probability of finding this particle in any interval of the x-axis is the same as that for any other interval of equal length and does not change with time. The plane wave is the simplest traveling waveform with this prop-

---

[1] The functional form for $\omega(k)$ was discussed in Section 5.3 for relativistic particles, where $E = \sqrt{(cp)^2 + (mc^2)^2}$. In the nonrelativistic case ($v \ll c$), this reduces to $E = p^2/2m + mc^2$. The rest energy $E_0 = mc^2$ can be disregarded in this case if we agree to make E_0 our energy reference. By measuring all energies from this level, we are in effect setting E_0 equal to zero.

[2] For a plane wave, the wave fronts (points of constant phase) constitute planes perpendicular to the direction of wave propagation. In the present case the constant phase requirement $kx - \omega t = constant$ demands only that x be fixed, so the wave fronts occupy the y–z planes.
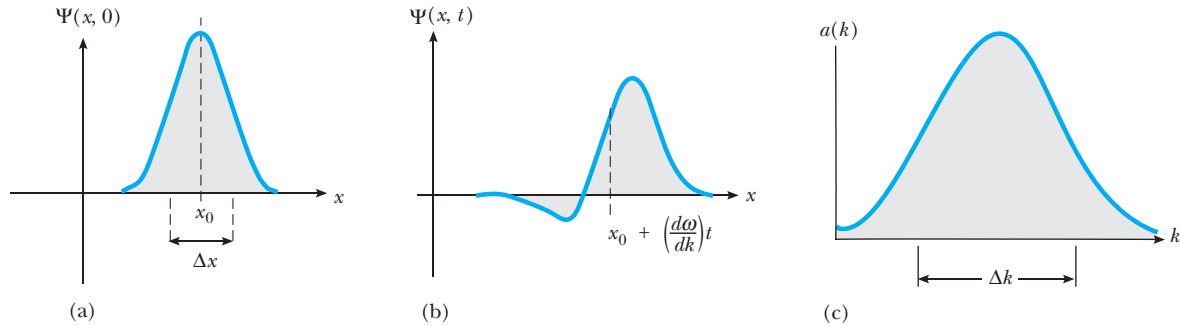
Figure 6.3 (a) A wave packet $\Psi(x, 0)$ formed from a superposition of plane waves. (b) The same wave packet some time t later (real part only). Because $v_p = \omega/k = \hbar k/2m$, the plane waves with smaller wavenumber move at slower speeds, and the packet becomes distorted. The body of the packet propagates with the group speed $d\omega/dk$ of the plane waves. (c) The amplitude distribution function $a(k)$ for this packet, indicating the amplitude of each plane wave in the superposition. A narrow wave packet requires a broad spectral content, and vice versa. That is, the widths Δx and Δk are inversely related as $\Delta x \Delta k \approx 1$.

erty—it expresses the reasonable notion that there are no special places for a free particle to be found. The particle's location is completely unknown at $t = 0$ and remains so for all time; however, its momentum and energy are known precisely as $p = \hbar k$ and $E = \hbar\omega$, respectively.

But not all free particles are described by Equation 6.6. For instance, we may establish (by measurement) that our particle initially is in some range Δx about x_0. In that case, $\Psi(x, 0)$ must be a *wave packet* concentrated in this interval, as shown in Figure 6.3a. The plane wave description is inappropriate now because the initial wave shape is not given correctly by $\Psi_k(x, 0) = e^{ikx}$. Instead, a sum of plane waves with different wavenumbers must be used to represent the packet. Because k is unrestricted, the sum actually is an integral here and we write

$$\Psi(x, 0) = \int_{-\infty}^{\infty} a(k)\, e^{ikx}\, dk \tag{6.7}$$

Representing a particle with a wave group

The coefficients $a(k)$ specify the amplitude of the plane wave with wavenumber k in the mixture and are chosen to reproduce the initial wave shape. For a given $\Psi(x, 0)$, the required $a(k)$ can be found from the theory of Fourier integrals. We shall not be concerned with the details of this analysis here; the essential point is that it can be done for a packet of any shape (see optional Section 5.4). If each plane wave constituting the packet is assumed to propagate independently of the others according to Equation 6.6, the packet at any time t is

$$\Psi(x, t) = \int_{-\infty}^{\infty} a(k)\, e^{i\{kx - \omega(k)t\}}\, dk \tag{6.8}$$

Notice that the initial data are used only to establish the amplitudes $a(k)$; subsequently, the packet develops according to the evolution of its plane wave constituents. Because each of these constituents moves with a different velocity $v_p = \omega/k$ (the phase velocity), the wave packet undergoes dispersion (see Section 5.3) and **the packet changes its shape as it propagates** (Fig. 6.3b). The speed of propagation of the wave packet as a whole is given by the group velocity $d\omega/dk$ of the plane waves forming the packet. Equation 6.8 no longer describes a

particle with precise values of momentum and energy. To construct a wave packet (that is, localize the particle), a mixture of wavenumbers (hence, particle momenta) is necessary, as indicated by the different $a(k)$. The amplitudes $a(k)$ furnish the so-called *spectral content* of the packet, which might look like that sketched in Figure 6.3c. The narrower the desired packet $\Psi(x, 0)$, the broader is the function $a(k)$ representing that packet. If Δx denotes the packet width and Δk the extent of the corresponding $a(k)$, one finds that the product always is a number of order unity, that is, $\Delta x \, \Delta k \approx 1$. Together with $p = \hbar k$, this implies an uncertainty principle:

$$\Delta x \, \Delta p \sim \hbar \tag{6.9}$$

EXAMPLE 6.3 Constructing a Wave Packet

Find the wavefunction $\Psi(x, 0)$ that results from taking the function $a(k) = (C\alpha/\sqrt{\pi})\exp(-\alpha^2 k^2)$, where C and α are constants. Estimate the product $\Delta x \, \Delta k$ for this case.

Solution The function $\Psi(x, 0)$ is given by the integral of Equation 6.7 or

$$\Psi(x, 0) = \int_{-\infty}^{\infty} a(k) e^{ikx} \, dk = \frac{C\alpha}{\sqrt{\pi}} \int_{-\infty}^{\infty} e^{(ikx - \alpha^2 k^2)} \, dk$$

To evaluate the integral, we first complete the square in the exponent as

$$ikx - \alpha^2 k^2 = -\left(\alpha k - \frac{ix}{2\alpha}\right)^2 - \frac{x^2}{4\alpha^2}$$

The second term on the right is constant for the integration over k; to integrate the first term we change variables with the substitution $z = \alpha k - ix/2\alpha$, obtaining

$$\Psi(x, 0) = \frac{C}{\sqrt{\pi}} e^{-x^2/4\alpha^2} \int_{-\infty}^{\infty} e^{-z^2} \, dz$$

The integral now is a standard one whose value is known to be $\sqrt{\pi}$. Then,

$$\Psi(x, 0) = Ce^{-x^2/4\alpha^2} = Ce^{-(x/2\alpha)^2}$$

This function $\Psi(x, 0)$, called a *Gaussian* function, has a single maximum at $x = 0$ and decays smoothly to zero on either side of this point (Fig. 6.4a). The width of this Gaussian packet becomes larger with increasing α. Accordingly, it is reasonable to identify α with Δx, the initial degree of localization. By the same token, $a(k)$ also is a Gaussian function, but with amplitude $C\alpha/\sqrt{\pi}$ and width $1/2\alpha$ (since $\alpha^2 k^2 = (k/2[1/2\alpha])^2$). Thus, $\Delta k = 1/2\alpha$ and $\Delta x \Delta k = 1/2$, *independent of α*. The multiplier C is a scale factor chosen to normalize Ψ.

Because our Gaussian packet is made up of many individual waves all moving with different speeds, the shape of the packet changes over time. In Problem 4 it is shown that the packet *disperses*, its width growing ever larger with the passage of time as

$$\Delta x(t) = \sqrt{[\Delta x(0)]^2 + \left[\frac{\hbar t}{2m\Delta x(0)}\right]^2}$$

Similarly, the peak amplitude diminishes steadily in order to keep the waveform normalized for all times (Fig. 6.4b). The wave as a whole does not propagate, because for every wavenumber k present in the wave group there is an equal admixture of the plane wave with the opposing wavenumber $-k$.
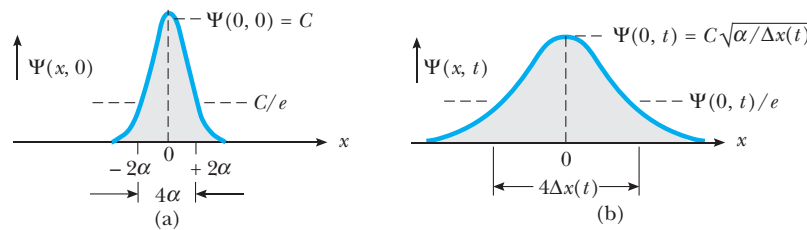

(a)

(b)

Figure 6.4 (Example 6.3) (a) The Gaussian wavefunction $\Psi(x, 0) = C\exp\{-(x/2\alpha)^2\}$, representing a particle initially localized around $x = 0$. C is the amplitude. At $x = \pm 2\alpha$, the amplitude is down from its maximum value by the factor $1/e$; accordingly, α is identified as the width of the Gaussian, $\alpha = \Delta x$. (b) The Gaussian wavefunction of Figure 6.4a at time t (apart from a phase factor). The width has increased to $\Delta x(t) = \sqrt{\alpha^2 + (\hbar t/2m\alpha)^2}$ and the amplitude is reduced by the factor $\sqrt{\alpha/\Delta x(t)}$.

EXAMPLE 6.4   Dispersion of Matter Waves

An atomic electron initially is localized to a region of space 0.10 nm wide (atomic size). How much time elapses before this localization is destroyed by dispersion? Repeat the calculation for a 1.0-g marble initially localized to 0.10 mm.

Solution   Taking for the initial state a Gaussian wave shape, we may use the results of the previous example. In particular, the extent of the matter wave after a time t has elapsed is

$$\Delta x(t) = \sqrt{[\Delta x(0)]^2 + \left[\frac{\hbar t}{2m\Delta x(0)}\right]^2}$$

where $\Delta x(0)$ is its initial width. The packet has effectively dispersed when $\Delta x(t)$ becomes appreciable compared to $\Delta x(0)$, say, $\Delta x(t) = 10\ \Delta x(0)$. This happens when $\hbar t/2m = \sqrt{99}\ [\Delta x(0)]^2$, or $t = \sqrt{99}\ (2m/\hbar)[\Delta x(0)]^2$.

The electron is initially localized to 0.10 nm ($= 10^{-10}$ m), and its mass is $m_e = 9.11 \times 10^{-31}$ kg. Thus, the electron wave packet disperses after a time

$$t = \sqrt{99}\left\{\frac{(2)(9.11 \times 10^{-31}\ \text{kg})}{1.055 \times 10^{-34}\,\text{J}\cdot\text{s}}\right\}(1.00 \times 10^{-10}\ \text{m})^2$$
$$= 1.7 \times 10^{-15}\ \text{s}$$

The same calculation for a 1.0-g marble localized to 0.10 mm $= 10^{-4}$ m gives

$$t = \sqrt{99}\left\{\frac{(2)(10^{-3}\ \text{kg})}{1.055 \times 10^{-34}\,\text{J}\cdot\text{s}}\right\}(10^{-4}\ \text{m})^2$$
$$= 1.9 \times 10^{24}\ \text{s}$$

or about 6.0×10^{16} years! This is nearly 10 million times the currently accepted value for the age of the Universe. With its much larger mass, the marble does not show the quantum effects of dispersion on any measurable time scale and will, for all practical purposes, remain localized "forever." By contrast, the localization of an atomic electron is destroyed in a time that is very short, on a par with the time it takes the electron to complete one Bohr orbit.

In closing this section, we note that *in principle* Equations 6.7 and 6.8 solve the fundamental problem of quantum mechanics for free particles subject to any initial condition $\Psi(x, 0)$. Because of its mathematical simplicity, the Gaussian wave packet is commonly used to represent the initial system state, as in the previous examples. However, the Gaussian form is often only an approximation to reality. Yet even in this simplest of cases, the mathematical challenge of obtaining $\Psi(x, t)$ from $\Psi(x, 0)$ tends to obscure the important results. Numerical simulation affords a convenient alternative to analytical calculation that also aids in visualizing the important phenomena of wave packet propagation and dispersion. To "see" quantum waveforms in action and further explore their time evolution, go to our companion Web site http://info.brookscole.com/mp3e, select QMTools Simulations → Evolution of Free Particle Wave Packets (Tutorial), and follow the on-site instructions.

6.3   WAVEFUNCTIONS IN THE PRESENCE OF FORCES

For a particle acted on by a force F, $\Psi(x, t)$ must be found from Schrödinger's equation:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + U(x)\Psi = i\hbar\frac{\partial\Psi}{\partial t} \tag{6.10}$$

The Schrödinger wave equation

Again, we assume knowledge of the initial wavefunction $\Psi(x, 0)$. In this expression, $U(x)$ is the potential energy function for the force F; that is,

$F = -dU/dx$. ==Schrödinger's equation is not derivable from any more basic principle, but is one of the laws of quantum physics. As with any law, its "truth" must be gauged ultimately by its ability to make predictions that agree with experiment.==

==**E**rwin Schrödinger== was an Austrian theoretical physicist best known as ==the creator of wave mechanics.== As a young man he was a good student who liked mathematics and physics, but also Latin and Greek for their logical grammar. He received a doctorate in physics from the University of Vienna. Although his work in physics was interrupted by World War I, Schrödinger had by 1920 produced important papers on statistical mechanics, color vision, and general relativity, which he at first found quite difficult to understand. Expressing his feelings about a scientific theory in the remarkably open and outspoken way he maintained throughout his life, Schrödinger found general relativity initially "depressing" and "unnecessarily complicated." Other Schrödinger remarks in this vein, with which some readers will enthusiastically agree, are as follows: The Bohr–Sommerfeld quantum theory was "unsatisfactory, even disagreeable." "I . . . feel intimidated, not to say repelled, by what seem to me the very difficult methods [of matrix mechanics] and by the lack of clarity."

Shortly after de Broglie introduced the concept of matter waves in 1924, Schrödinger began to develop a new relativistic atomic theory based on de Broglie's ideas, but his failure to include electron spin led to the failure of this theory for hydrogen. By January of 1926, however, by treating the electron as a nonrelativistic particle, Schrödinger had introduced his famous wave equation and successfully obtained the energy values and wavefunctions for hydrogen. As Schrödinger himself pointed out, an outstanding fea-

Image not available due to copyright restrictions

ERWIN SCHRÖDINGER
(1887–1961)

ture of his approach was that the discrete energy values emerged from his wave equation in a natural way (as in the case of standing waves on a string), and in a way superior to the artificial postulate approach of Bohr. Another outstanding feature of Schrödinger's wave mechanics was that it was easier to apply to physical problems than Heisenberg's matrix mechanics, because it involved a partial differential equation very similar to the classical wave equation. Intrigued by the remarkable differences in conception and mathematical method of wave and matrix mechanics, Schrödinger did much to hasten the universal acceptance of all of quantum theory by demonstrating the mathematical equivalence of the two theories in 1926.

Although Schrödinger's wave theory was generally based on clear physical ideas, one of its major problems in 1926 was the physical interpretation of the wavefunction Ψ. Schrödinger felt that the electron was ultimately a wave, Ψ was the vibration amplitude of this wave, and $\Psi^*\Psi$ was the electric charge density. As mentioned in Chapter 4, Born, Bohr, Heisenberg, and others pointed out the problems with this interpretation and presented the currently accepted view that $\Psi^*\Psi$ is a probability and that the electron is ultimately no more a wave than a particle. Schrödinger never accepted this view, but registered his "concern and disappointment" that this "transcendental, almost psychical interpretation" had become "universally accepted dogma."

==In 1927, Schrödinger, at the invitation of Max Planck, accepted the chair of theoretical physics at the University of Berlin, where he formed a close friendship with Planck and experienced six stable and productive years.== In 1933, disgusted with the Nazis like so many of his colleagues, he left Germany. After several moves reflecting the political instability of Europe, he eventually settled at the Dublin Institute for Advanced Studies. Here he spent 17 happy, creative years working on problems in general relativity, cosmology, and the application of quantum physics to biology. This last effort resulted in a fascinating short book, *What is Life?*, which induced many young physicists to investigate biological processes with chemical and physical methods. In 1956, he returned home to his beloved Tyrolean mountains. He died there in 1961.

The Schrödinger equation propagates the initial wave forward in time. To see how this works, suppose $\Psi(x, 0)$ has been given. Then the left-hand side (LHS) of Schrödinger's equation can be evaluated and Equation 6.10 gives $\partial\Psi/\partial t$ at $t = 0$, the initial rate of change of the wavefunction. From this we compute the wavefunction a short time, δt, later as $\Psi(x, \delta t) = \Psi(x, 0) + [\partial\Psi/\partial t]_0 \delta t$. This allows the LHS to be re-evaluated, now at $t = \delta t$. With each such repetition, Ψ is advanced another step δt into the future. Continuing the process generates Ψ at any later time t. Such repetitious calculations are ideally suited to computers, and the method just outlined may be used to solve the Schrödinger equation numerically.[3]

But how can we obtain an explicit mathematical expression for $\Psi(x, t)$? Returning to the free particle case, we see that the plane waves $\Psi_k(x, t)$ of Equation 6.6 serve a dual purpose: On the one hand, they represent particles whose momentum (hence, energy) is known precisely; on the other, they become the building blocks for constructing wavefunctions satisfying any initial condition. From this perspective, the question naturally arises: Do analogous functions exist when forces are present? The answer is yes! To obtain them we look for solutions to the Schrödinger equation having the separable form[4]

$$\Psi(x, t) = \psi(x)\phi(t) \tag{6.11}$$

where $\psi(x)$ is a function of x only and $\phi(t)$ is a function of t only. (Note that the plane waves have just this form, with $\psi(x) = e^{ikx}$ and $\phi(t) = e^{-i\omega t}$.) Substituting Equation 6.11 into Equation 6.10 and dividing through by $\psi(x)\phi(t)$ gives

$$-\frac{\hbar^2}{2m}\frac{\psi''(x)}{\psi(x)} + U(x) = i\hbar\frac{\phi'(t)}{\phi(t)}$$

where primes denote differentiation with respect to the arguments. Now the LHS of this equation is a function of x only,[5] and the RHS is a function of t only. Since we can assign any value of x independently of t, the two sides of the equation can be equal only if each is equal to the same constant, which we call E.[6] This yields two equations determining the unknown functions $\psi(x)$ and $\phi(t)$. The resulting equation for the time-

---

[3]This straightforward approach suffers from numerical instabilities and does not, for example, conserve probability. In practice, a more sophisticated discretization scheme is usually employed, such as that provided by the Crank–Nicholson method. See, for example, section 17.2 of *Numerical Recipes* by W. H. Press, B. P. Flannery, S. A. Teukolsky, W. T. Vetterling, Cambridge, U.K., Cambridge University Press, 1986.

[4]Obtaining solutions to partial differential equations in separable form is called *separation of variables*. On separating variables, a partial differential equation in, say, N variables is reduced to N ordinary differential equations, each involving only a single variable. The technique is a general one which may be applied to many (but not all!) of the partial differential equations encountered in science and engineering applications.

[5]Implicitly we have assumed that the potential energy $U(x)$ is a function of x only. For potentials that also depend on t (for example, those arising from a time-varying electric field), solutions to the Schrödinger equation in separable form generally do not exist.

[6]More explicitly, changing t cannot affect the LHS because this depends only on x. Since the two sides of the equation are equal, we conclude that changing t cannot affect the RHS either. It follows that the RHS must reduce to a constant. The same argument with x replacing t shows the LHS also must reduce to this same constant.

dependent function $\phi(t)$ is

$$i\hbar \frac{d\phi}{dt} = E\phi(t) \tag{6.12}$$

This can be integrated immediately to give $\phi(t) = e^{-i\omega t}$ with $\omega = E/\hbar$. Thus, the time dependence is the same as that obtained for free particles! The equation for the space function $\psi(x)$ is

Wave equation for matter waves in separable form

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + U(x)\psi(x) = E\psi(x) \tag{6.13}$$

Equation 6.13 is called the **time-independent Schrödinger equation.** Explicit solutions to this equation cannot be written for an arbitrary potential energy function $U(x)$. But whatever its form, $\psi(x)$ must be well behaved because of its connection with probabilities. In particular, $\psi(x)$ must be everywhere finite, single-valued, and continuous. Furthermore, $\psi(x)$ must be "smooth," that is, the slope of the wave $d\psi/dx$ also must be continuous wherever $U(x)$ has a finite value.[7]

For free particles we take $U(x) = 0$ in Equation 6.13 (to give $F = -dU/dx = 0$) and find that $\psi(x) = e^{ikx}$ is a solution with $E = \hbar^2 k^2/2m$. Thus, for free particles the separation constant E becomes the total particle energy; this identification continues to be valid when forces are present. The wavefunction $\psi(x)$ will change, however, with the introduction of forces, because particle momentum (hence, k) is no longer constant.

The separable solutions to Schrödinger's equation describe conditions of particular physical interest. One feature shared by all such wavefunctions is especially noteworthy: Because $|e^{-i\omega t}|^2 = e^{+i\omega t}e^{-i\omega t} = e^0 = 1$, we have

$$|\Psi(x, t)|^2 = |\psi(x)|^2 \tag{6.14}$$

This equality expresses the time independence of all probabilities calculated from $\Psi(x, t)$. For this reason, solutions in separable form are called **stationary states.** Thus, **for stationary states all probabilities are static** and can be calculated from the time-independent wavefunction $\psi(x)$.

6.4   THE PARTICLE IN A BOX

Of the problems involving forces, the simplest is that of particle confinement. Consider a particle moving along the x-axis between the points $x = 0$ and $x = L$, where L is the length of the "box." Inside the box the particle is free; at the endpoints, however, it experiences strong forces that serve to

---

[7]On rearrangement, the Schrödinger equation specifies the second derivative of the wavefunction $d^2\psi/dx^2$ at any point as

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

It follows that if $U(x)$ is finite at x, the second derivative also is finite here and the slope $d\psi/dx$ will be continuous.

contain it. A simple example is a ball bouncing elastically between two impenetrable walls (Fig. 6.5). A more sophisticated one is a charged particle moving along the axis of aligned metallic tubes held at different potentials, as shown in Figure 6.6a. The central tube is grounded, so a test charge inside this tube has zero electric potential energy and experiences no electric force. When both outer tubes are held at a high electric potential V, there are no electric fields within them, but strong repulsive fields arise in the gaps at 0 and L. The potential energy $U(x)$ for this situation is sketched in Figure 6.6b. As V is increased without limit and the gaps are simultaneously reduced to zero, we approach the idealization known as the *infinite square well*, or "box" potential (Fig. 6.6c).
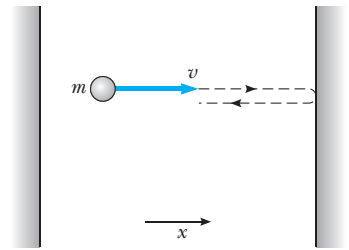
From a classical viewpoint, our particle simply bounces back and forth between the confining walls of the box. Its speed remains constant, as does its kinetic energy. Furthermore, classical physics places no restrictions on the values of its momentum and energy. The quantum description is quite different and leads to the interesting phenomenon of energy quantization.

We are interested in the time-independent wavefunction $\psi(x)$ of our particle. Because it is confined to the box, the particle can never be found outside, which requires ψ to be zero in the exterior regions $x < 0$ and $x > L$. Inside the box, $U(x) = 0$ and Equation 6.13 for $\psi(x)$ becomes, after rearrangement,

$$\frac{d^2\psi}{dx^2} = -k^2\psi(x) \quad \text{with} \quad k^2 = \frac{2mE}{\hbar^2}$$

Independent solutions to this equation are sin kx and cos kx, indicating that k is the wavenumber of oscillation. The most general solution is a linear

Figure 6.5   A particle of mass m and speed v bouncing elastically between two impenetrable walls.
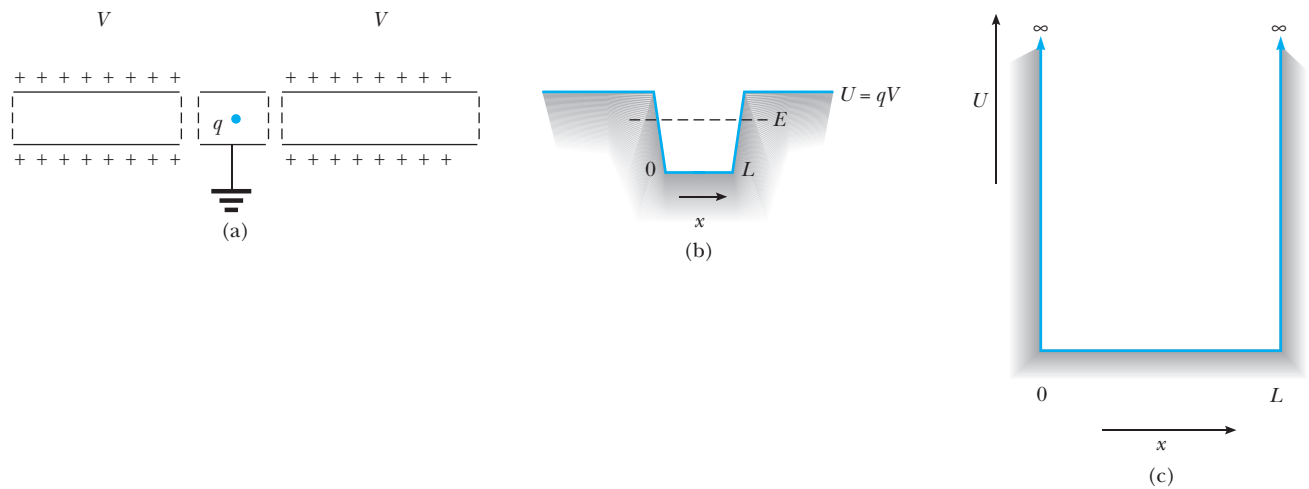

(a)

(b)

(c)

Figure 6.6   (a) Aligned metallic cylinders serve to confine a charged particle. The inner cylinder is grounded, while the outer ones are held at some high electric potential V. A charge q moves freely within the cylinders, but encounters electric forces in the gaps separating them. (b) The electric potential energy seen by this charge. A charge whose total energy is less than qV is confined to the central cylinder by the strong repulsive forces in the gaps at $x = 0$ and $x = L$. (c) As V is increased and the gaps between cylinders are narrowed, the potential energy approaches that of the infinite square well.
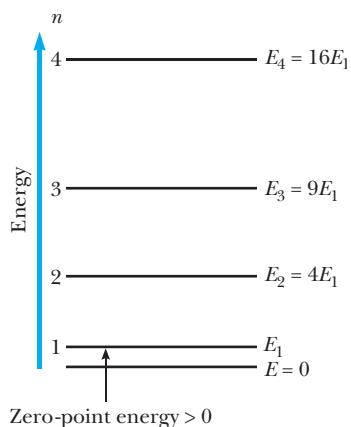
Figure 6.7 Energy-level diagram for a particle confined to a one-dimensional box of width L. The lowest allowed energy is E_1, with value $\pi^2\hbar^2/2mL^2$.

Allowed energies for a particle in a box

combination of these two,

$$\psi(x) = A\sin kx + B\cos kx \qquad \text{for } 0 < x < L \qquad (6.15)$$

This interior wave must match the exterior wave at the walls of the box for $\psi(x)$ to be continuous everywhere.[8] Thus, we require the interior wave to vanish at $x = 0$ and $x = L$:

$$\psi(0) = B = 0 \qquad \text{(continuity at } x = 0\text{)}$$
$$\psi(L) = A\sin kL = 0 \qquad \text{(continuity at } x = L\text{)} \qquad (6.16)$$

The last condition requires that $kL = n\pi$, where n is any positive integer.[9] Because $k = 2\pi/\lambda$, this is equivalent to fitting an integral number of half-wavelengths into the box (see Fig. 6.9a). Using $k = n\pi/L$, we find that the particle energies are *quantized*, being restricted to the values

$$E_n = \frac{\hbar^2 k^2}{2m} = \frac{n^2\pi^2\hbar^2}{2mL^2} \qquad n = 1, 2, \ldots \qquad (6.17)$$

The lowest allowed energy is given by $n = 1$ and is $E_1 = \pi^2\hbar^2/2mL^2$. This is the **ground state.** Because $E_n = n^2E_1$, the **excited states** for which $n = 2, 3, 4, \ldots$ have energies $4E_1, 9E_1, 16E_1, \ldots$ An energy-level diagram is given in Figure 6.7. Notice that $E = 0$ is not allowed; that is, *the particle can never be at rest.* The least energy the particle can have, E_1, is called the **zero-point energy.** This result clearly contradicts the classical prediction, for which $E = 0$ is an acceptable energy, as are all positive values of E. The following example illustrates how this contradiction is reconciled with our everyday experience.

EXAMPLE 6.5   Energy Quantization for a Macroscopic Object

A small object of mass 1.00 mg is confined to move between two rigid walls separated by 1.00 cm. (a) Calculate the minimum speed of the object. (b) If the speed of the object is 3.00 cm/s, find the corresponding value of n.

Solution   Treating this as a particle in a box, the energy of the particle can only be one of the values given by Equation 6.17, or

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

The minimum energy results from taking $n = 1$. For $m = 1.00$ mg and $L = 1.00$ cm, we calculate

$$E_1 = \frac{(6.626 \times 10^{-34}\,\text{J}\cdot\text{s})^2}{8.00 \times 10^{-10}\,\text{kg}\cdot\text{m}^2} = 5.49 \times 10^{-58}\,\text{J}$$

Because the energy is all kinetic, $E_1 = mv_1^2/2$ and the minimum speed v_1 of the particle is

$$v_1 = \sqrt{2(5.49 \times 10^{-58}\,\text{J})/(1.00 \times 10^{-6}\,\text{kg})}$$
$$= 3.31 \times 10^{-26}\,\text{m/s}$$

This speed is immeasurably small, so that for practical purposes the object can be considered to be at rest. Indeed, the time required for an object with this speed to move the 1.00 cm separating the walls is about

---

[8]Although $\psi(x)$ must be continuous everywhere, the slope of $d\psi/dx$ is *not* continuous at the walls of the box, where $U(x)$ becomes infinite (cf. footnote 7).

[9]For $n = 0$ $(E = 0)$, Schrödinger's equation requires $d^2\psi/dx^2 = 0$, whose solution is given by $\psi(x) = Ax + B$ for some choice of constants A and B. For this wavefunction to vanish at $x = 0$ and $x = L$, both A and B must be zero, leaving $\psi(x) = 0$ everywhere. In such a case the particle is nowhere to be found; that is, no description is possible when $E = 0$. Also, the inclusion of negative integers $n < 0$ produces no new states, because changing the sign of n merely changes the sign of the wavefunction, leading to the same probabilities as for positive integers.

3×10^{23} s, or about 1 million times the present age of the Universe! It is reassuring to verify that quantum mechanics applied to macroscopic objects does not contradict our everyday experiences.

If, instead, the speed of the particle is $v = 3.00$ cm/s, then its energy is

$$E = \frac{mv^2}{2} = \frac{(1.00 \times 10^{-6} \text{ kg})(3.00 \times 10^{-2} \text{ m/s})^2}{2}$$

$$= 4.50 \times 10^{-10} \text{ J}$$

This, too, must be one of the special values E_n. To find which one, we solve for the quantum number n, obtaining

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

$$= \frac{\sqrt{(8.00 \times 10^{-10} \text{ kg} \cdot \text{m}^2)(4.50 \times 10^{-10} \text{ J})}}{6.626 \times 10^{-34} \text{ J} \cdot \text{s}}$$

$$= 9.05 \times 10^{23}$$

Notice that the quantum number representing a typical speed for this ordinary-size object is enormous. In fact, the value of n is so large that we would never be able to distinguish the quantized nature of the energy levels. That is, the difference in energy between two consecutive states with quantum numbers $n_1 = 9.05 \times 10^{23}$ and $n_2 = 9.05 \times 10^{23} + 1$ is only about 10^{-33} J, much too small to be detected experimentally. This is another example that illustrates the working of Bohr's correspondence principle, which asserts that quantum predictions must agree with classical results for large masses and lengths.

EXAMPLE 6.6   Model of an Atom

An atom can be viewed as a number of electrons moving around a positively charged nucleus, where the electrons are subject mainly to the Coulombic attraction of the nucleus (which actually is partially "screened" by the intervening electrons). The potential well that each electron "sees" is sketched in Figure 6.8. Use the model of a particle in a box to estimate the energy (in eV) required to raise an atomic electron from the state $n = 1$ to the state $n = 2$, assuming the atom has a radius of 0.100 nm.

Solution   Taking the length L of the box to be 0.200 nm (the diameter of the atom), $m_e = 511$ keV/c^2, and $\hbar c = 197.3$ eV·nm for the electron, we calculate
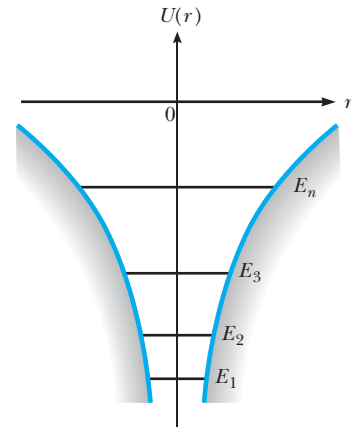

Figure 6.8   (Example 6.6) Model of the potential energy versus r for the one-electron atom.

$$E_1 = \frac{\pi^2 \hbar^2}{2m_e L^2}$$

$$= \frac{\pi^2 (197.3 \text{ eV} \cdot \text{nm}/c)^2}{2(511 \times 10^3 \text{ eV}/c^2)(0.200 \text{ nm})^2}$$

$$= 9.40 \text{ eV}$$

and

$$E_2 = (2)^2 E_1 = 4(9.40 \text{ eV}) = 37.6 \text{ eV}$$

Therefore, the energy that must be supplied to the electron is

$$\Delta E = E_2 - E_1 = 37.6 \text{ eV} - 9.40 \text{ eV} = 28.2 \text{ eV}$$

We could also calculate the wavelength of the photon that would cause this transition by identifying ΔE with the photon energy hc/λ, or

$$\lambda = hc/\Delta E = (1.24 \times 10^3 \text{ eV} \cdot \text{nm})/(28.2 \text{ eV}) = 44.0 \text{ nm}$$

This wavelength is in the far ultraviolet region, and it is interesting to note that the result is roughly correct. Although this oversimplified model gives a good estimate for transitions between lowest-lying levels of the atom, the estimate gets progressively worse for higher-energy transitions.

Exercise 1   Calculate the minimum speed of an atomic electron modeled as a particle in a box with walls that are 0.200 nm apart.

Answer 1.82×10^6 m/s.

Returning to the wavefunctions, we have from Equation 6.15 (with $k = n\pi/L$ and $B = 0$)

Stationary states for a particle in a box

$$\psi_n(x) = A \sin\left(\frac{n\pi x}{L}\right) \qquad \text{for } 0 < x < L \text{ and } n = 1, 2, \ldots \qquad (6.18)$$

For each value of the quantum number *n* there is a specific wavefunction $\psi_n(x)$ describing the state of the particle with energy E_n. Figure 6.9 shows plots of ψ_n versus x and of the probability density $|\psi_n|^2$ versus x for $n = 1$, 2, and 3, corresponding to the three lowest allowed energies for the particle. For $n = 1$, the probability of finding the particle is largest at $x = L/2$—this is the *most probable position* for a particle in this state. For $n = 2$, $|\psi|^2$ is a maximum at $x = L/4$ and again at $x = 3L/4$: Both points are equally likely places for a particle in this state to be found.

There are also points within the box where it is impossible to find the particle. Again for $n = 2$, $|\psi|^2$ is zero at the midpoint, $x = L/2$; for $n = 3$, $|\psi|^2$ is zero at $x = L/3$ and at $x = 2L/3$, and so on. But this raises an interesting question: How does our particle get from one place to another when there is no probability for its ever being at points in between? It is as if there were *no path at all*, and not just that the probabilities $|\psi|^2$ express our ignorance about a world somehow hidden from view. Indeed, what is at stake here is the very essence of a particle as something that gets from one place to another by occupying all intervening positions. The objects of quantum mechanics are not particles, but more complicated things having both particle *and wave* attributes.

Actual probabilities can be computed only after ψ_n is normalized, that is, we must be sure that all probabilities sum to unity:

$$1 = \int_{-\infty}^{\infty} |\psi_n(x)|^2 \, dx = A^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx$$
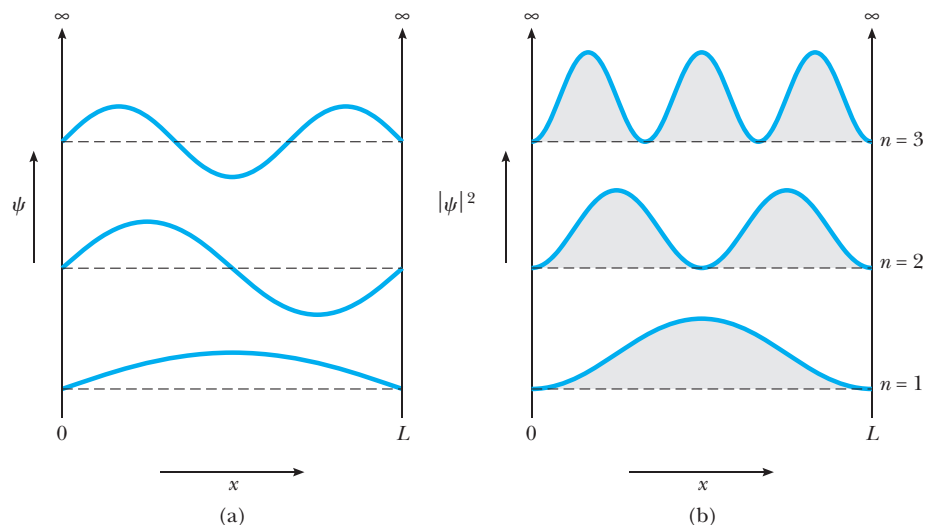

Figure 6.9 The first three allowed stationary states for a particle confined to a one-dimensional box. (a) The wavefunctions for $n = 1$, 2, and 3. (b) The probability distributions for $n = 1$, 2, and 3.

The integral is evaluated with the help of the trigonometric identity $2 \sin^2\theta = 1 - \cos 2\theta$:

$$\int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx = \frac{1}{2}\int_0^L [1 - \cos(2n\pi x/L)] \, dx$$

Only the first term contributes to the integral, because the cosine integrates to $\sin(2n\pi x/L)$, which vanishes at the limits 0 and L. Thus, normalization requires $1 = A^2 L/2$, or

$$A = \sqrt{\frac{2}{L}} \qquad\qquad (6.19)$$

EXAMPLE 6.7   Probabilities for a Particle in a Box

A particle is known to be in the ground state of an infinite square well with length L. Calculate the probability that this particle will be found in the middle half of the well, that is, between $x = L/4$ and $x = 3L/4$.

Solution   The probability density is given by $|\psi_n|^2$ with $n = 1$ for the ground state. Thus, the probability is

$$P = \int_{L/4}^{3L/4} |\psi_1|^2 \, dx = \left(\frac{2}{L}\right)\int_{L/4}^{3L/4} \sin^2(\pi x/L) \, dx$$

$$= \left(\frac{1}{L}\right)\int_{L/4}^{3L/4} [1 - \cos(2\pi x/L)] \, dx$$

$$= \left(\frac{1}{L}\right)\left[\frac{L}{2} - \left(\frac{L}{2\pi}\right)\sin(2\pi x/L)\Big|_{L/4}^{3L/4}\right]$$

$$= \frac{1}{2} - \left(\frac{1}{2\pi}\right)[-1 - 1] = 0.818$$

Notice that this is considerably larger than $\frac{1}{2}$, which would be expected for a classical particle that spends equal time in all parts of the well.

Exercise 2   Repeat the calculation of Example 6.7 for a particle in the nth state of the infinite square well, and show that the result approaches the classical value $\frac{1}{2}$ in the limit $n \rightarrow \infty$.

Charge-Coupled Devices (CCDs)

Potential wells are essential to the operation of many modern electronic devices, though rarely is the well shape so simple that it can be accurately modeled by the infinite square well discussed in this section. The charge-coupled device, or CCD, uses potential wells to trap electrons and create a faithful electronic reproduction of light intensity across the active surface.

For more than two decades now, CCDs have been helping astronomers see amazing detail in distant galaxies using much shorter exposure times than with traditional photographic emulsions (Fig. 6.10). These devices consist of a two-dimensional array of moveable electron boxes (or wells) created beneath a set of electrodes formed on the surface of a thin silicon chip (Fig. 6.11). The silicon serves the dual purpose of emitting an electron when struck by a photon and acting as a local trap for electrons. The potential energy seen by an electron in this environment is shown by the curve on the right in Figure 6.11, with the depth coordinate increasing downward. Though far removed from a

Figure 6.10 Researchers at Arizona State University, using NASA's Hubble Space Telescope, believe they are seeing the conclusion of the cosmic epoch where the young galaxies started to shine in significant numbers, about 13 billion years ago. The image shows some of the objects that the team discovered using Hubble's new Advanced Camera for Surveys (ACS), based on CCD technology. Astronomers believe that these numerous objects are faint young star-forming galaxies seen when the universe was seven times smaller than it is today (at redshifts of about 6) and less than a billion years old. (*H-J. Yan, R. Windhorst and S. Cohen, Arizona State University and NASA*).

"box" potential, the well shape nevertheless serves to confine the emitted electrons in the depth dimension. [Each well or picture element (pixel) in the array also is isolated electrically from its neighbors, in effect confining the electrons in the remaining two dimensions perpendicular to the figure.] The number of electrons in a given well, and consequently the number of photons striking a particular point on the chip, may be read out electronically and the signal processed by computer to enhance the image. The name "charge-coupled device" was coined to describe the way the signals are read from the individual wells. A row of wells containing trapped electrons is moved vertically one step at a time by changing the voltage on the vertical electrodes in a progressive manner. When a row reaches the output register, the pixels are moved horizontally by systematically changing the voltage on the horizontal electrodes. In this way an entire row is read out in serial fashion by an amplifier at the end of the output register. Figure 6.12 illustrates the operating principle. CCD development has been impressive over the past two decades, and currently square arrays of over 4 million pixels (2048 pixels on a side) packed into a chip of several square centimeters are available. An entire CCD sensor is shown in Figure 6.13a; Figure 6.13b shows the cross section of a single pixel in a CCD image sensor, enlarged 5000 times.

CCD imagers possess several advantages over other light detectors. Because CCDs detect as many as 90% of the photons hitting their surface, they are far more sensitive than the best photographic emulsions, which can detect only 2–3% of those bone-weary photons that have traveled millions of lightyears from distant galaxies. In addition, CCDs can accurately measure the exact brightness of an object, since their voltage output is directly proportional to light input over a very wide brightness range. Another great feature of CCDs is their ability to measure accurately both faint and bright objects in the same frame. This is not true for photographic emulsions, where bright objects wash out faint details. Faint objects are recorded by cooling the CCD with liquid nitrogen to keep competing thermally generated electrons (noise) to a minimum. The simultaneous measurement of bright images is limited only by the filling of potential wells with electrons. State-of-the-art CCDs can hold as many as 100,000 electrons in a single well and are about 100 times better than photographic plates at simultaneously recording bright and faint objects. The ability to record where an incident photon strikes also is important for locating the exact position of a faint star. CCDs afford exceptional geometric accuracy because each pixel position is defined by the rigid physical structure of the

Figure 6.11 Structure of a single picture element (pixel) in a CCD array. The sketch on the right shows how the potential energy of an electron varies with depth in the device.
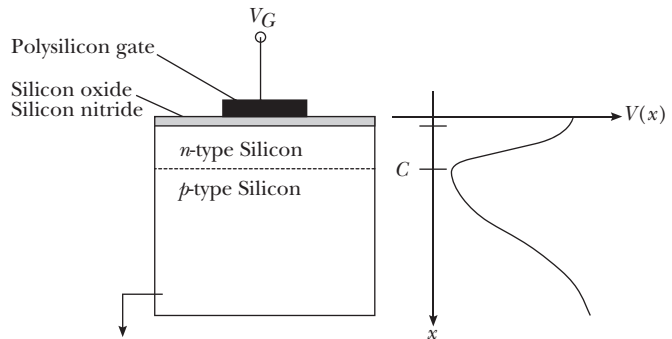
Image not available due to copyright restrictions

Images not available due to copyright restrictions

chip. (Because of their high resolution and geometric accuracy, CCDs also are used to record the paths of energetic elementary particles by collecting the electrons generated along their tracks.) Finally, overall noise and signal

Image not available due to copyright restrictions
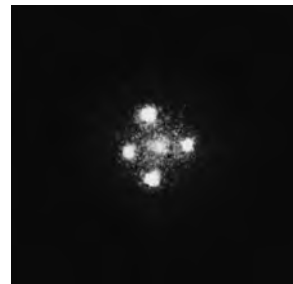
(b)

Figure 6.14   The "clover leaf," the quadruply lensed quasar H1413+117. The four images of comparable brightness are only 1 arcsec apart. The spectra of two of the images are identical, except for some absorption lines in one that presumably come from different gas clouds that are in the other's line of sight. The redshift is 2.55. The rare configuration and identical spectra show that we are seeing gravitational lensing rather than a cluster of quasars.

(b) A Hubble Space Telescope view, in which the lensing galaxy is revealed. (*NASA/ESA*)

degradation have decreased so markedly in CCDs that as many as 99.9999% of the electrons are transferred in each well shift. This is crucial since image readout involves thousands of such transfers.

Figure 6.14a shows a remarkable quadruply lensed quasar. The multiple images result when light from a single quasar is deflected by gravitational forces as it passes near an intervening galaxy on its journey to Earth. Figure 16.14b shows the lensing galaxy, beautifully resolved by the CCD imager on board the Hubble Space Telescope. These, and similar images offer conclusive proof of the superior ability of CCDs to make extremely accurate position measurements of faint objects in the presence of much brighter ones.

6.5   THE FINITE SQUARE WELL

The "box" potential is an oversimplification that is never realized in practice. Given sufficient energy, a particle can escape the confines of any well. The potential energy for a more realistic situation—the finite square well—is shown in Figure 6.15, and essentially is that depicted in Figure 6.6b before taking the limit $V \rightarrow \infty$. A classical particle with energy E greater than the well height U can penetrate the gaps at $x = 0$ and $x = L$ to enter the outer region. Here it moves freely, but with reduced speed corresponding to a diminished kinetic energy $E - U$.

A classical particle with energy E less than U is permanently bound to the region $0 < x < L$. Quantum mechanics asserts, however, that there is some probability that the particle can be found *outside* this region! That is, the wavefunction generally is nonzero outside the well, and so the probability of finding the particle here also is nonzero. For stationary states, the wavefunction $\psi(x)$ is found from the time-independent Schrödinger equation. Outside the well where $U(x) = U$, this is

$$\frac{d^2\psi}{dx^2} = \alpha^2\psi(x) \qquad x < 0 \text{ and } x > L$$

with $\alpha^2 = 2m(U - E)/\hbar^2$ a constant. Because $U > E$, α^2 necessarily is positive and the independent solutions to this equation are the *real* exponentials $e^{+\alpha x}$ and $e^{-\alpha x}$. The positive exponential must be rejected in region III where $x > L$ to keep $\psi(x)$ finite as $x \rightarrow \infty$; likewise, the negative exponential must be rejected in region I where $x < 0$ to keep $\psi(x)$ finite as $x \rightarrow -\infty$. Thus, the exterior wave takes the form

$$\psi(x) = Ae^{+\alpha x} \qquad \text{for } x < 0$$
$$\psi(x) = Be^{-\alpha x} \qquad \text{for } x > L$$

(6.20)

The coefficients A and B are determined by matching this wave smoothly onto the wavefunction in the well interior. Specifically, we require $\psi(x)$ and its first derivative $d\psi/dx$ to be continuous at $x = 0$ and again at $x = L$. This can be done only for certain values of E, corresponding to the allowed energies for the bound particle. For these energies, the matching conditions specify the entire wavefunction except for a multiplicative constant, which then is determined by normalization. Figure 6.16 shows the wavefunctions and probability densities that result for the three lowest allowed particle energies. Note that in each case the waveforms join smoothly at the boundaries of the potential well.

The fact that ψ is nonzero at the walls *increases* the de Broglie wavelength in the well (compared with that in the infinite well), and this in turn lowers the energy and momentum of the particle. This observation can be used to approximate the

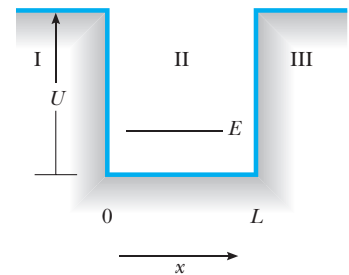**Figure 6.15** Potential-energy diagram for a well of finite height U and width L. The energy E of the particle is less than U.
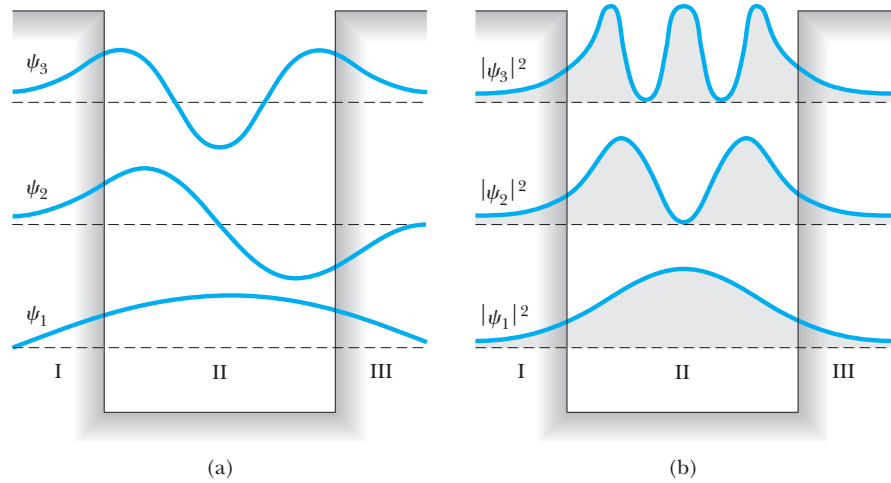
(a)   (b)

Figure 6.16   (a) Wavefunctions for the lowest three energy states for a particle in a potential well of finite height. (b) Probability densities for the lowest three energy states for a particle in a potential well of finite height.

allowed energies for the bound particle.[10] The wavefunction penetrates the exterior region on a scale of length set by the **penetration depth** δ, given by

Penetration depth

$$\delta = \frac{1}{\alpha} = \frac{\hbar}{\sqrt{2m(U - E)}} \qquad (6.21)$$

Specifically, at a distance δ beyond the well edge, the wave amplitude has fallen to $1/e$ of its value at the edge and approaches zero exponentially in the exterior region. That is, the exterior wave is essentially zero beyond a distance δ on either side of the potential well. If it were truly zero beyond this distance, the allowed energies would be those for an infinite well of length $L + 2\delta$ (compare Equation 6.17), or

Approximate energies for a particle in a well of finite height

$$E_n \approx \frac{n^2 \pi^2 \hbar^2}{2m(L + 2\delta)^2} \qquad n = 1, 2, \ldots \qquad (6.22)$$

The allowed energies for a particle bound to the finite well are given approximately by Equation 6.22 so long as δ is small compared with L. But δ itself is energy dependent according to Equation 6.21. Thus, Equation 6.22 becomes an implicit relation for E that must be solved numerically for a given value of n. The approximation is best for the lowest-lying states and breaks down completely as E approaches U, where δ becomes infinite. From this we infer (correctly) that the number of bound states is limited by the height U of our potential well. Particles with energies E exceeding U are not bound to the well, that is, they may be found with comparable probability in the exterior regions. The case of unbound states will be taken up in the following chapter.

[10]This specific approximation method was reported by S. Garrett in the *Am. J. Phys.* 47:195–196, 1979.

EXAMPLE 6.8   A Bound Electron

Estimate the ground-state energy for an electron confined to a potential well of width 0.200 nm and height 100 eV.

Solution   We solve Equations 6.21 and 6.22 together, using an iterative procedure. Because we expect $E \ll U(= 100 \text{ eV})$, we estimate the decay length δ by first neglecting E to get

$$\delta \approx \frac{\hbar}{\sqrt{2mU}} = \frac{(197.3 \text{ eV} \cdot \text{nm}/c)}{\sqrt{2(511 \times 10^3 \text{ eV}/c^2)(100 \text{ eV})}}$$
$$= 0.0195 \text{ nm}$$

Thus, the effective width of the (infinite) well is $L + 2\delta = 0.239$ nm, for which we calculate the ground-state energy:

$$E \approx \frac{\pi^2(197.3 \text{ eV} \cdot \text{nm}/c)^2}{2(511 \times 10^3 \text{ eV}/c^2)(0.239 \text{ nm})^2} = 6.58 \text{ eV}$$

From this E we calculate $U - E = 93.42$ eV and a new decay length

$$\delta \approx \frac{(197.3 \text{ eV} \cdot \text{nm}/c)}{\sqrt{2(511 \times 10^3 \text{ eV}/c^2)(93.42 \text{ eV})}} = 0.0202 \text{ nm}$$

This, in turn, increases the effective well width to 0.240 nm and lowers the ground-state energy to $E = 6.53$ eV. The iterative process is repeated until the desired accuracy is achieved. Another iteration gives the same result to the accuracy reported. This is in excellent agreement with the exact value, about 6.52 eV for this case.

Exercise 3   Bound-state waveforms and allowed energies for the finite square well also can be found using purely numerical methods. Go to our companion Web site (http://info.brookscole.com/mp3e) and select QMTools Simulations → Exercise 6.3. The applet shows the potential energy for an electron confined to a finite well of width 0.200 nm and height 100 eV. Follow the on-site instructions to add a stationary wave and determine the energy of the ground state. Repeat the procedure for the first excited state. Compare the symmetry and the number of nodes for these two wavefunctions. Find the highest-lying bound state for this finite well. Count nodes to determine which excited state this is, and thus deduce the total number of bound states this well supports.

EXAMPLE 6.9   Energy of a Finite Well: Exact Treatment

Impose matching conditions on the interior and exterior wavefunctions and show how these lead to energy quantization for the finite square well.

Solution   The exterior wavefunctions are the decaying exponential functions given by Equation 6.20 with decay constant $\alpha = [2m(U - E)/\hbar^2]^{1/2}$. The interior wave is an oscillation with wavenumber $k = (2mE/\hbar^2)^{1/2}$ having the same form as that for the infinite well, Equation 6.15; here we write it as

$$\psi(x) = C \sin kx + D \cos kx \qquad \text{for } 0 < x < L$$

To join this smoothly onto the exterior wave, we insist that the wavefunction and its slope be continuous at the well edges $x = 0$ and $x = L$. At $x = 0$ the conditions for smooth joining require

$$A = D \qquad \text{(continuity of } \psi \text{)}$$

$$\alpha A = kC \qquad \left(\text{continuity of } \frac{d\psi}{dx} \right)$$

Dividing the second equation by the first eliminates A, leaving

$$\frac{C}{D} = \frac{\alpha}{k}$$

In the same way, smooth joining at $x = L$ requires

$$C \sin kL + D \cos kL = Be^{-\alpha L} \qquad \text{(continuity of } \psi \text{)}$$

$$kC \cos kL - kD \sin kL = -\alpha Be^{-\alpha L} \qquad \left(\text{continuity of } \frac{d\psi}{dx} \right)$$

Again dividing the second equation by the first eliminates B. Then replacing C/D with α/k gives

$$\frac{(\alpha/k)\cos kL - \sin kL}{(\alpha/k)\sin kL + \cos kL} = -\frac{\alpha}{k}$$

For a specified well height U and width L, this last relation can only be satisfied for special values of E (E is contained in both k and α). For any other energies, the waveform will not match smoothly at the well edges, leaving a wavefunction that is physically inadmissable. (Note that the equation cannot be solved explicitly for E; rather, solutions must be obtained using numerical or graphical methods.)

Exercise 4   Use the result of Example 6.9 to verify that the ground-state energy for an electron confined to a square well of width 0.200 nm and height 100 eV is about 6.52 eV.

6.6 THE QUANTUM OSCILLATOR

As a final example of a potential well for which exact results can be obtained, let us examine the problem of a particle subject to a linear restoring force $F = -Kx$. Here x is the displacement of the particle from equilibrium ($x = 0$) and K is the force constant. The corresponding potential energy is given by $U(x) = \frac{1}{2}Kx^2$. The prototype physical system fitting this description is a mass on a spring, but the mathematical description actually applies to any object limited to small excursions about a point of stable equilibrium.

Consider the general potential function sketched in Figure 6.17. The positions a, b, and c all label equilibrium points where the force $F = -dU/dx$ is zero. Further, positions a and c are examples of *stable* equilibria, but b is *unstable*. The stability of equilibrium is decided by examining the forces in the immediate neighborhood of the equilibrium point. Just to the left of a, for example, $F = -dU/dx$ is positive, that is, the force is directed to the right; conversely, to the right of a the force is directed to the left. Therefore, a particle displaced slightly from equilibrium at a encounters a force driving it back to the equilibrium point (restoring force). Similar arguments show that the equilibrium at c also is stable. On the other hand, a particle displaced in either direction from point b experiences a force that drives it further away from equilibrium—an unstable condition. In general, stable and unstable equilibria are marked by potential curves that are concave or convex, respectively, at
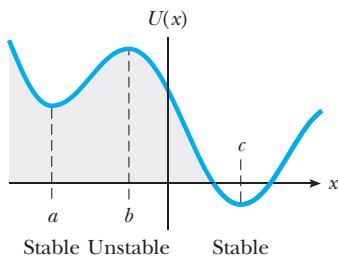

Figure 6.17 A general potential function $U(x)$. The points labeled a and c are positions of stable equilibrium, for which $dU/dx = 0$ and $d^2U/dx^2 > 0$. Point b is a position of unstable equilibrium, for which $dU/dx = 0$ and $d^2U/dx^2 < 0$.

the equilibrium point. To put it another way, **the curvature of $U(x)$ is positive ($d^2U/dx^2 > 0$) at a point of stable equilibrium, and negative ($d^2U/dx^2 < 0$) at a point of unstable equilibrium.**

Near a point of stable equilibrium such as a (or c), $U(x)$ can be fit quite well by a parabola:

$$U(x) = U(a) + \tfrac{1}{2}K(x - a)^2 \tag{6.23}$$

Of course, the curvature of this parabola ($= K$) must match that of $U(x)$ at the equilibrium point $x = a$:

$$K = \left.\frac{d^2U}{dx^2}\right|_a \tag{6.24}$$

Further, $U(a)$, the potential energy at equilibrium, may be taken as zero if we agree to make this our energy reference, that is, if we subsequently measure all energies from this level. In the same spirit, the coordinate origin may be placed at $x = a$, in effect allowing us to set $a = 0$. With $U(a) = 0$ and $a = 0$, Equation 6.23 becomes the spring potential once again; in other words, **a particle limited to small excursions about any stable equilibrium point behaves as if it were attached to a spring with a force constant K prescribed by the curvature of the true potential at equilibrium.** In this way the oscillator becomes a first approximation to the vibrations occurring in many real systems.

Harmonic approximation to vibrations occurring in real systems

The motion of a classical oscillator with mass m is simple harmonic vibration at the angular frequency $\omega = \sqrt{K/m}$. If the particle is removed from equilibrium a distance A and released, it oscillates between the points $x = -A$ and $x = +A$ (A is the amplitude of vibration), with total energy $E = \tfrac{1}{2}KA^2$. By changing the initial point of release A, the classical particle can in principle be given any (nonnegative) energy whatsoever, including zero.

The quantum oscillator is described by the potential energy $U(x) = \tfrac{1}{2}Kx^2 = \tfrac{1}{2}m\omega^2x^2$ in the Schrödinger equation. After a little rearrangement we get

$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2}\left(\frac{1}{2}m\omega^2x^2 - E\right)\psi(x) \tag{6.25}$$

as the equation for the stationary states of the oscillator. The mathematical technique for solving this equation is beyond the level of this text. (The exponential and trigonometric forms for ψ employed previously will not work here because of the presence of x^2 in the potential.) It is instructive, however, to make some intelligent guesses and verify their accuracy by direct substitution. The ground-state wavefunction should possess the following attributes:

1. ψ should be *symmetric* about the midpoint of the potential well $x = 0$.
2. ψ should be *nodeless*, but approaching zero for $|x|$ large.

Both expectations are derived from our experience with the lowest energy states of the infinite and finite square wells, which you might want to review at this time. The symmetry condition (1) requires ψ to be some function of x^2; further, the function must have no zeros (other than at infinity) to meet the nodeless requirement (2). The simplest choice fulfilling both demands is the Gaussian form

$$\psi(x) = C_0e^{-\alpha x^2} \tag{6.26}$$

$\psi_0(x)$

(a)

$|\psi_0(x)|^2$

(b)

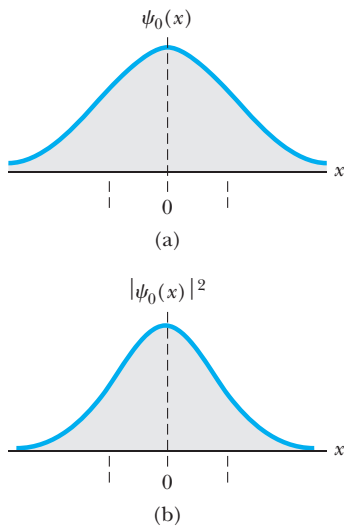**Figure 6.18** (a) Wavefunction for the ground state of a particle in the oscillator potential well. (b) The probability density for the ground state of a particle in the oscillator potential well. The dashed vertical lines mark the limits of vibration for a classical particle with the same energy, $x = \pm A = \pm\sqrt{\hbar/m\omega}$.

for some as-yet-unknown constants C_0 and α. Taking the second derivative of $\psi(x)$ in Equation 6.26 gives (as you should verify)

$$\frac{d^2\psi}{dx^2} = \{4\alpha^2 x^2 - 2\alpha\}C_0 e^{-\alpha x^2} = \{4\alpha^2 x^2 - 2\alpha\}\psi(x)$$

which has the same structure as Equation 6.25. Comparing like terms between them, we see that we have a solution provided that both

$$4\alpha^2 = \frac{2m}{\hbar^2}\frac{1}{2}m\omega^2 \qquad \text{or} \qquad \alpha = \frac{m\omega}{2\hbar} \tag{6.27}$$

and

$$\frac{2mE}{\hbar^2} = 2\alpha = \frac{m\omega}{\hbar} \qquad \text{or} \qquad E = \tfrac{1}{2}\hbar\omega \tag{6.28}$$

In this way we discover that the oscillator ground state is described by the wavefunction $\psi_0(x) = C_0 \exp(-m\omega x^2/2\hbar)$ and that the energy of this state is $E_0 = \tfrac{1}{2}\hbar\omega$. The constant C_0 is reserved for normalization (see Example 6.10). The ground-state wave ψ_0 and associated probability density $|\psi_0|^2$ are illustrated in Figure 6.18. The dashed vertical lines mark the limits of vibration for a classical oscillator with the same energy. Note the considerable penetration of the wave into the classically forbidden regions $x > A$ and $x < -A$. A detailed analysis shows that the particle can be found in these nonclassical regions about 16% of the time (see Example 6.12).

EXAMPLE 6.10 Normalizing the Oscillator Ground State Wavefunction

Normalize the oscillator ground-state wavefunction found in the preceding paragraph.

Solution With $\psi_0(x) = C_0 e^{-m\omega x^2/2\hbar}$, the integrated probability is

$$\int_{-\infty}^{\infty} |\psi_0(x)|^2\, dx = C_0^2 \int_{-\infty}^{\infty} e^{-m\omega x^2/\hbar}\, dx$$

Evaluation of the integral requires advanced techniques. We shall be content here simply to quote the formula

$$\int_{-\infty}^{\infty} e^{-ax^2}\, dx = \sqrt{\frac{\pi}{a}} \qquad a > 0$$

In our case we identify a with $m\omega/\hbar$ and obtain

$$\int_{-\infty}^{\infty} |\psi_0(x)|^2\, dx = C_0^2 \sqrt{\frac{\pi\hbar}{m\omega}}$$

Normalization requires this integrated probability to be 1, leading to

$$C_0 = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}$$

EXAMPLE 6.11 Limits of Vibration for a Classical Oscillator

Obtain the limits of vibration for a classical oscillator having the same total energy as the quantum oscillator in its ground state.

Solution The ground-state energy of the quantum oscillator is $E_0 = \tfrac{1}{2}\hbar\omega$. At its limits of vibration $x = \pm A$, the classical oscillator has transformed all this energy into elastic potential energy of the spring, given by $\tfrac{1}{2}KA^2 = \tfrac{1}{2}m\omega^2 A^2$. Therefore,

$$\tfrac{1}{2}\hbar\omega = \tfrac{1}{2}m\omega^2 A^2 \qquad \text{or} \qquad A = \sqrt{\frac{\hbar}{m\omega}}$$

The classical oscillator vibrates in the interval given by $-A \leq x \leq A$, having insufficient energy to exceed these limits.

EXAMPLE 6.12 The Quantum Oscillator in the Nonclassical Region

Calculate the probability that a quantum oscillator in its ground state will be found outside the range permitted for a classical oscillator with the same energy.

Solution Because the classical oscillator is confined to the interval $-A \leq x \leq A$, where A is its amplitude of vibration, the question is one of finding the quantum oscillator outside this interval. From the previous example we have $A = \sqrt{\hbar/m\omega}$ for a classical oscillator with energy $\frac{1}{2}\hbar\omega$. The quantum oscillator with this energy is described by the wavefunction $\psi_0(x) = C_0\exp(-m\omega x^2/2\hbar)$, with $C_0 = (m\omega/\pi\hbar)^{1/4}$ from Example 6.10. The probability in question is found by integrating the probability density $|\psi_0|^2$ in the region beyond the classical limits of vibration, or

$$P = \int_{-\infty}^{-A} |\psi_0|^2 \, dx + \int_{A}^{\infty} |\psi_0|^2 \, dx$$

From the symmetry of ψ_0, the two integrals contribute equally to P, so

$$P = 2\left(\frac{m\omega}{\pi\hbar}\right)^{1/2} \int_{A}^{\infty} e^{-m\omega x^2/\hbar} \, dx$$

Changing variables from x to $z = \sqrt{m\omega/\hbar}\ x$ and using $A = \sqrt{\hbar/m\omega}$ (corresponding to $z = 1$) leads to

$$P = \frac{2}{\sqrt{\pi}} \int_{1}^{\infty} e^{-z^2} \, dz$$

Expressions of this sort are encountered frequently in probability studies. With the lower limit of integration changed to a variable—say, y—the result for P defines the *complementary error function* erfc(y). Values of the error function may be found in tables. In this way we obtain $P = \text{erfc}(1) = 0.157$, or about 16%.

To obtain excited states of the oscillator, a procedure can be followed similar to that for the ground state. The first excited state should be antisymmetric about the midpoint of the oscillator well ($x = 0$) and display exactly one node. By virtue of the antisymmetry, this node must occur at the origin, so that a suitable trial solution would be $\psi(x) = x \exp(-\alpha x^2)$. Substituting this form into Equation 6.25 yields the same α as before, along with the first excited-state energy $E_1 = \frac{3}{2}\hbar\omega$.

Continuing in this manner, we could generate ever-higher-lying oscillator states with their respective energies, but the procedure rapidly becomes too laborious to be practical. What is needed is a systematic approach, such as that provided by the method of power series expansion.[11] Pursuing this method would take us too far afield, but the result for the allowed oscillator energies is quite simple and sufficiently important that it be included here:

$$E_n = (n + \tfrac{1}{2})\hbar\omega \qquad n = 0, 1, 2, \ldots. \qquad (6.29)$$

The energy-level diagram following from Equation 6.29 is given in Figure 6.19. Note the uniform spacing of levels, widely recognized as the hallmark of the harmonic oscillator spectrum. The energy difference between adjacent levels is just $\Delta E = \hbar\omega$. In these results we find the quantum justification for Planck's revolutionary hypothesis concerning his cavity resonators (see Section 3.2). In deriving his blackbody radiation formula, Planck assumed that these resonators (oscillators), which made up the cavity walls, could possess only those energies that were multiples of $hf = \hbar\omega$. Although Planck could not have foreseen the zero-point energy $\hbar\omega/2$, it would make no difference: His resonators still would emit or absorb light energy in the bundles $\Delta E = hf$ necessary to reproduce the blackbody spectrum.

Energy levels for the harmonic oscillator
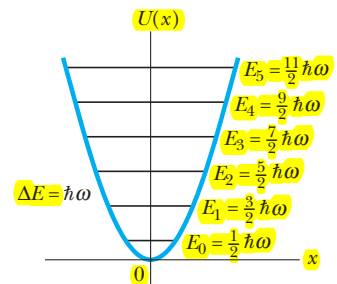
Figure 6.19 Energy-level diagram for the quantum oscillator. Note that the levels are equally spaced, with a separation equal to $\hbar\omega$. The ground state energy is E_0.

[11]The method of power series expansion as applied to the problem of the quantum oscillator is developed in any more advanced quantum mechanics text. See, for example, E. E. Anderson, *Modern Physics and Quantum Mechanics*, Philadelphia, W. B. Saunders Company, 1971.
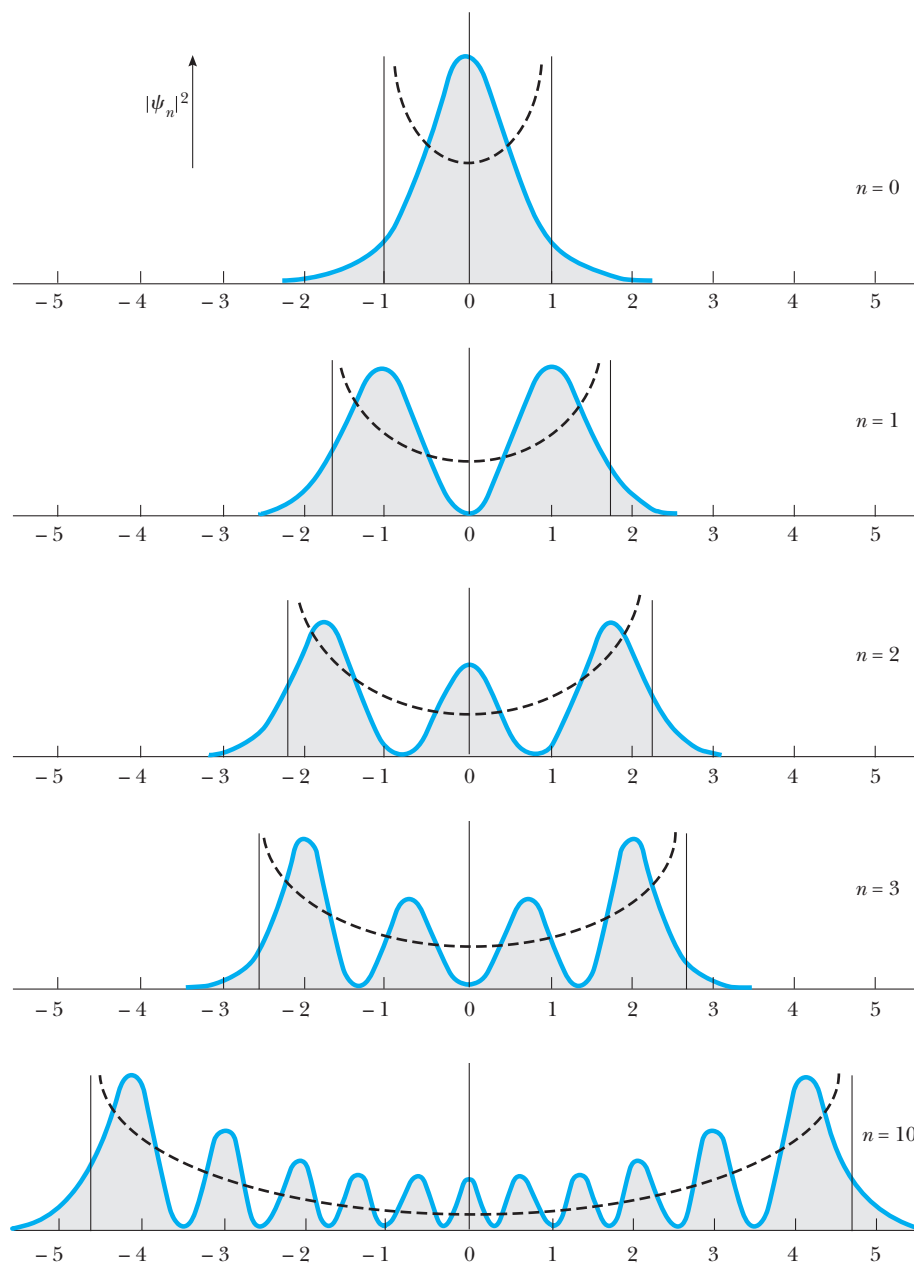
Figure 6.20 Probability densities for a few states of the quantum oscillator. The dashed curves represent the classical probabilities corresponding to the same energies.

The probability densities for some of the oscillator states are plotted in Figure 6.20. The dashed lines, representing the classical probability densities for the same energy, are provided for comparison (see Problem 28 for the calculation of classical probabilities). Note that as n increases, agreement between the classical and quantum probabilities improves, as expected from the correspondence principle.

EXAMPLE 6.13   Quantization of Vibrational Energy

The energy of a quantum oscillator is restricted to be one of the values $(n + \frac{1}{2})\hbar\omega$. How can this quantization apply to the motion of a mass on a spring, which seemingly can vibrate with any amplitude (energy) whatever?

Solution   The discrete values for the allowed energies of the oscillator would go unnoticed if the spacing between adjacent levels were too small to be detected. At the macroscopic level, a laboratory mass m of, say, 0.0100 kg on a spring having force constant $K = 0.100$ N/m (a typical value) would oscillate with angular frequency $\omega = \sqrt{K/m} = 3.16$ rad/s. The corresponding period of vibration is $T = 2\pi/\omega = 1.99$ s. In this case the quantum level spacing is only

$$\Delta E = \hbar\omega = (6.582 \times 10^{-16} \text{ eV·s})(3.16 \text{ rad/s})$$
$$= 2.08 \times 10^{-15} \text{ eV}$$

Such small energies are far below present limits of detection.

At the atomic level, however, much higher frequencies are commonplace. Consider the vibrational frequency of the hydrogen molecule. This behaves as an oscillator with $K = 510.5$ N/m and reduced mass $\mu = 8.37 \times 10^{-28}$ kg. The angular frequency of oscillation is therefore

$$\omega = \sqrt{\frac{K}{\mu}} = \sqrt{\frac{510.5 \text{ N/m}}{8.37 \times 10^{-28} \text{ kg}}}$$
$$= 7.81 \times 10^{14} \text{ rad/s}$$

At such frequencies, the quantum of energy $\hbar\omega$ is 0.513 eV, which can be measured easily!

6.7   EXPECTATION VALUES

It should be evident by now that two distinct types of measurable quantities are associated with a given wavefunction $\Psi(x, t)$. One type—like the energy E for the stationary states—is fixed by the quantum number labeling the wave. Therefore, every measurement of this quantity performed on the system described by Ψ yields the *same* value. Quantities such as E we call **sharp** to distinguish them from others—like the position x—for which the wavefunction Ψ furnishes only probabilities. We say x is an example of a dynamic quantity that is **fuzzy.** In the following paragraphs we discuss what more can be learned about these "fuzzy" quantities.

Sharp and fuzzy variables

A particle described by the wavefunction Ψ may occupy various places x with probability given by the wave intensity there, $|\Psi(x)|^2$. Predictions made this way from Ψ can be tested by making repeated measurements of the particle position. Table 6.1 shows results that might be obtained in a hypothetical experiment of this sort. The table consists of 18 entries, each one representing the actual position of the particle recorded in that particular measurement. We see that the

Table 6.1   Hypothetical Data Set for Position of a Particle as Recorded in Repeated Trials

Trial	Position (arbitrary units)	Trial	Position (arbitrary units)	Trial	Position (arbitrary units)
1	$x_1 = 2.5$	7	$x_7 = 8.0$	13	$x_{13} = 4.2$
2	$x_2 = 3.7$	8	$x_8 = 6.4$	14	$x_{14} = 8.8$
3	$x_3 = 1.4$	9	$x_9 = 4.1$	15	$x_{15} = 6.2$
4	$x_4 = 7.9$	10	$x_{10} = 5.4$	16	$x_{16} = 7.1$
5	$x_5 = 6.2$	11	$x_{11} = 7.0$	17	$x_{17} = 5.4$
6	$x_6 = 5.4$	12	$x_{12} = 3.3$	18	$x_{18} = 5.3$

entry 5.4 occurs most often (in 3 of the 18 trials); it represents the most probable position based on the data available. The probability associated with this position, again based on the available data, is $3/18 = 0.167$. These numbers will fluctuate as additional measurements are taken, but they should approach limiting values. The theoretical predictions refer to these limiting values. A good test of the theory would require much more data than we have shown in this illustration.

The information in Table 6.1 also can be used to find the average position of the particle:

$$\overline{x} = \frac{(2.5 + 3.7 + 1.4 + \cdots + 5.4 + 5.3)}{18} = 5.46$$

This same number can be found in a different way. First, order the table entries by value, starting with the smallest: 1.4, 2.5, 3.3, ..., 5.4, 6.2, ..., 8.0, 8.8. Now take each value, multiply by its frequency of occurrence, and sum the results:

$$1.4 \left(\frac{1}{18}\right) + 2.5 \left(\frac{1}{18}\right) + \cdots + 5.4 \left(\frac{3}{18}\right)$$

$$+ 6.2 \left(\frac{2}{18}\right) + \cdots + 8.8 \left(\frac{1}{18}\right) = 5.46$$

The two procedures are equivalent, but the latter involves a sum over *ordered values* rather than individual table entries. We may generalize this last expression to include other values for the position of the particle, provided we weight each one by its observed frequency of occurrence (in this case, zero). This allows us to write a general prescription to calculate the average particle position from any data set:

$$\overline{x} = \sum x P_x \tag{6.30}$$

The sum now includes all values of x, each weighted by its frequency or probability of occurrence P_x. Because the possible values of x are distributed continuously over the entire range of real numbers, the sum in Equation 6.30 really should be an integral and P_x should refer to the probability of finding the particle in the infinitesimal interval dx about the point x; that is, the probability $P_x \rightarrow P(x)\,dx$, where $P(x)$ is the probability density. In quantum mechanics, $P(x) = |\Psi|^2$ and the average value of x, written in quantum mechanics as $\langle x \rangle$, is called the **expectation value.** Then,

Average position of a particle

$$\langle x \rangle = \int_{-\infty}^{\infty} x |\Psi(x, t)|^2 \, dx \tag{6.31}$$

Notice that $\langle x \rangle$ may be a function of time. For a stationary state, however, $|\Psi|^2$ is static and, as a consequence, $\langle x \rangle$ is independent of t.

In similar fashion we find that the average or expectation value for any function of x, say $f(x)$, is

$$\langle f \rangle = \int_{-\infty}^{\infty} f(x) |\Psi|^2 \, dx \tag{6.32}$$

With $f(x) = U(x)$, Equation 6.32 becomes $\langle U \rangle$, the average potential energy of the particle. With $f(x) = x^2$, the quantum uncertainty in particle position may

be found. To see how this is done, we return to Table 6.1 and notice that the entries scatter about the average value. The amount of scatter is measured by the standard deviation, σ, of the data, defined as

$$\sigma = \sqrt{\frac{\Sigma(x_i - \overline{x})^2}{N}} \tag{6.33}$$

where N is the number of data points—in this case, 18. Writing out the square under the radical gives

$$\frac{\Sigma(x_i)^2}{N} - 2(\overline{x})\frac{\Sigma(x_i)}{N} + (\overline{x})^2\Sigma\left(\frac{1}{N}\right) = \overline{(x^2)} - 2(\overline{x})(\overline{x}) + (\overline{x})^2$$

$$= \overline{(x^2)} - (\overline{x})^2$$

and so

$$\sigma = \sqrt{\overline{(x^2)} - (\overline{x})^2}$$

From Equation 6.33 we see that if the standard deviation were zero, all data entries would be identical and equal to the average. In that case the distribution is *sharp;* otherwise, the data exhibit some spread (as in Table 6.1) and the standard deviation is greater than zero. In quantum mechanics the standard deviation, written Δx, is often called the *uncertainty* in position. The preceding development implies that the quantum uncertainty in position can be calculated from expectation values as

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} \tag{6.34}$$

The degree to which particle position is fuzzy is given by the magnitude of Δx; note that the position is sharp only if $\Delta x = 0$.

EXAMPLE 6.14   Standard Deviation from Averages

Compute $\overline{(x^2)}$ and the standard deviation for the data given in Table 6.1.

Solution Squaring the data entries of Table 6.1 and adding the results gives $\Sigma(x_i)^2 = 603.91$. Dividing this by the number of data points, $N = 18$, we find $\overline{(x^2)} = 603.91/18 = 33.55$. Then,

$$\sigma = \sqrt{33.55 - (5.46)^2} = 1.93$$

for this case.

EXAMPLE 6.15   Location of a Particle in a Box

Compute the average position $\langle x \rangle$ and the quantum uncertainty in this value, Δx, for the particle in a box, assuming it is in the ground state.

Solution The possible particle positions within the box are weighted according to the probability density given by $|\Psi|^2 = (2/L)\sin^2(n\pi x/L)$, with $n = 1$ for the ground state. The average position is calculated as

$$\langle x \rangle = \int_{-\infty}^{\infty} x|\Psi|^2\, dx = \left(\frac{2}{L}\right)\int_0^L x\sin^2\left(\frac{\pi x}{L}\right) dx$$

Making the change of variable $\theta = \pi x/L$ (so that $d\theta = \pi\, dx/L$) gives

$$\langle x \rangle = \frac{2L}{\pi^2}\int_0^\pi \theta\sin^2\theta\, d\theta$$

The integral is evaluated with the help of the trigonometric identity $2\sin^2\theta = 1 - \cos 2\theta$, giving

$$\langle x \rangle = \frac{L}{\pi^2}\left(\int_0^\pi \theta\, d\theta - \int_0^\pi \theta\cos 2\theta\, d\theta\right)$$

An integration by parts shows that the second integral vanishes, whereas the first integrates to $\pi^2/2$. Thus, the average particle position is the midpoint $\langle x \rangle = L/2$ as expected, because there is equal probability of finding the particle in the left half or the right half of the box.

$\langle x^2 \rangle$ is computed in much the same way, but with an extra factor of x in the integrand. After changing variables to $\theta = \pi x/L$, we get

$$\langle x^2 \rangle = \frac{L^2}{\pi^3}\left(\int_0^\pi \theta^2\, d\theta - \int_0^\pi \theta^2\cos 2\theta\, d\theta\right)$$

The first integral evaluates to $\pi^3/3$; the second may be integrated twice by parts to get

$$\int_0^\pi \theta^2 \cos 2\theta \, d\theta = -\int_0^\pi \theta \sin 2\theta \, d\theta$$

$$= \frac{1}{2} \theta \cos 2\theta \big|_0^\pi = \pi/2$$

Then,

$$\langle x^2 \rangle = \frac{L^2}{\pi^3} \left(\frac{\pi^3}{3} - \frac{\pi}{2} \right) = \frac{L^2}{3} - \frac{L^2}{2\pi^2}$$

Finally, the uncertainty in position for this particle is

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = L\sqrt{\frac{1}{3} - \frac{1}{2\pi^2} - \frac{1}{4}} = 0.181L$$

This is an appreciable figure, amounting to nearly one-fifth the size of the box. Consequently, the whereabouts of such a particle are largely unknown. With some confidence, we may assert only that the particle is likely to be in the range $L/2 \pm 0.181L$.

Finally, notice that none of these results depends on the time, because in a stationary state t enters only through the exponential factor $e^{-i\omega t}$, which cancels when Ψ is combined with Ψ^* in the calculation of averages. Therefore, it is generally true that, **in a stationary state, all averages, as well as probabilities, are time independent.**

We have learned how to predict the average position of a particle, $\langle x \rangle$; the uncertainty in this position, Δx; the average potential energy of the particle, $\langle U \rangle$; and so on. But what about the average momentum $\langle p \rangle$ of the particle or its average kinetic energy $\langle K \rangle$? These could be calculated if $p(x)$, the momentum as a function of x, were known. In classical mechanics, $p(x)$ may be obtained from the equation for the classical path taken by the particle, $x(t)$. Differentiating this function once gives the velocity $v(t)$. Then inverting $x(t)$ to get t as a function of x, and substituting this result into $v(t)$, gives $v(x)$ and the desired relation $p(x) = mv(x)$. In quantum mechanics, however, x and t are independent variables—*there is no path,* nor any function connecting p with x! If there were, then p could be found from x using $p(x)$ and both x and p would be known precisely, in violation of the uncertainty principle.

To obtain $\langle p \rangle$ we must try a different approach: We identify the time derivative of the average particle position with the average velocity of the particle. After multiplication by m, this gives the average momentum $\langle p \rangle$:

Average momentum of a particle

$$\langle p \rangle = m \frac{d\langle x \rangle}{dt} \tag{6.35}$$

Equation 6.35 cannot be derived from anything we have said previously. When applied to macroscopic objects where the quantum uncertainties in position and momentum are small, the averages $\langle x \rangle$ and $\langle p \rangle$ become indistinguishable from "the" position and "the" momentum of the object, and Equation 6.35 reduces to the classical definition of momentum.

An equivalent expression for $\langle p \rangle$ follows from Equation 6.35 by substituting $\langle x \rangle$ from Equation 6.31 and differentiating under the integral sign. Using Schrödinger's equation to eliminate time derivatives of Ψ and its conjugate Ψ^* gives (after much manipulation!)

$$\langle p \rangle = \int_{-\infty}^{\infty} \Psi^* \left(\frac{\hbar}{i} \right) \frac{\partial \Psi}{\partial x} \, dx \tag{6.36}$$

Exercise 5 Show that $\langle p \rangle = 0$ for *any* state of a particle in a box.

6.8   OBSERVABLES AND OPERATORS

An observable is any particle property that can be measured. The position and momentum of a particle are observables, as are its kinetic and potential energies.[12] In quantum mechanics, we associate an *operator* with each of these observables. Using this operator, one can calculate the average value of the corresponding observable. An operator here refers to an operation to be performed on whatever function follows the operator. The quantity operated on is called the *operand*. In this language a constant c becomes an operator, whose meaning is understood by supplying any function $f(x)$ to obtain $cf(x)$. Here the operator c means "multiplication by the constant c." A more complicated operator is d/dx, which, after supplying an operand $f(x)$, means "take the derivative of $f(x)$ with respect to x." Still another example is $(d/dx)^2 = (d/dx)(d/dx)$. Supplying the operand $f(x)$ gives $(d/dx)^2 f(x) = (d/dx)(df/dx) = d^2 f/dx^2$. Hence, $(d/dx)^2$ means "take the second derivative with respect to x, that is, take the indicated derivative twice."

The operator concept is useful in quantum mechanics because all expectation values we have encountered so far can be written in the same general form, namely,

$$\langle Q \rangle = \int_{-\infty}^{\infty} \Psi^* [Q] \Psi \, dx \qquad (6.37)$$

Operators in quantum mechanics

In this expression, Q is the observable and $[Q]$ is the associated operator. *The order of terms in Equation 6.37 is important;* it indicates that the operand for $[Q]$ always is Ψ. Comparing the general form with that for $\langle p \rangle$ in Equation 6.36 shows that the momentum operator is $[p] = (\hbar/i)(\partial/\partial x)$. Similarly, writing $x|\Psi|^2 = \Psi^* x \Psi$ in Equation 6.31 implies that the operator for position is $[x] = x$. From $[x]$ and $[p]$ the operator for any other observable can be found. For instance, the operator for x^2 is just $[x^2] = [x]^2 = x^2$. For that matter, the operator for potential energy is simply $[U] = U([x]) = U(x)$, meaning that average potential energy is computed as

$$\langle U \rangle = \int_{-\infty}^{\infty} \Psi^* [U] \Psi \, dx = \int_{-\infty}^{\infty} \Psi^* U(x) \Psi \, dx$$

Still another example is the kinetic energy K. Classically, K is a function of p: $K = p^2/2m$. Then the kinetic energy operator is $[K] = ([p])^2/2m = (-\hbar/2m)\partial^2/\partial x^2$, and average kinetic energy is found from

$$\langle K \rangle = \int_{-\infty}^{\infty} \Psi^* [K] \Psi \, dx = \int_{-\infty}^{\infty} \Psi^* \left(-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} \right) dx$$

To find the average total energy for a particle, we sum the average kinetic and potential energies to get

$$\langle E \rangle = \langle K \rangle + \langle U \rangle = \int_{-\infty}^{\infty} \Psi^* \left\{ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U(x) \right\} \Psi \, dx \qquad (6.38)$$

---

[12]By contrast, the wavefunction Ψ, although clearly indispensable to the quantum description, is not directly measurable and so is *not* an observable.

Table 6.2 Common Observables and Associated Operators

Observable	Symbol	Associated Operator
Position	x	x
Momentum	p	$\dfrac{\hbar}{i}\dfrac{\partial}{\partial x}$
Potential energy	U	$U(x)$
Kinetic energy	K	$-\dfrac{\hbar^2}{2m}\dfrac{\partial^2}{\partial x^2}$
Hamiltonian	H	$-\dfrac{\hbar^2}{2m}\dfrac{\partial^2}{\partial x^2}+U(x)$
Total energy	E	$i\hbar\dfrac{\partial}{\partial t}$

The form of this result suggests that the term in the braces is the operator for total energy. This operator is called the *Hamiltonian,* symbolized by $[H]$:

$$[H] = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x) \tag{6.39}$$

The designation $[E]$ is reserved for another operator, which arises as follows: Inspection of Schrödinger's equation (Equation 6.10) shows that it can be written neatly as $[H]\Psi = i\hbar\partial\Psi/\partial t$. Using this in Equation 6.38 gives an equivalent expression for $\langle E\rangle$ and leads to the identification of the *energy operator*:

$$[E] = i\hbar\frac{\partial}{\partial t} \tag{6.40}$$

Notice that $[H]$ is an operation involving only the spatial coordinate x, whereas $[E]$ depends only on the time t. That is, $[H]$ and $[E]$ really are two different operators, but they produce identical results when applied to any solution of Schrödinger's equation. This is because the LHS of Schrödinger's equation is simply $[H]\Psi$, while the RHS is none other than $[E]\Psi$ (compare Equation 6.10)! Table 6.2 summarizes the observables we have discussed and their associated operators.

O P T I O N A L

QUANTUM UNCERTAINTY AND THE EIGENVALUE PROPERTY

In Section 6.7 we showed how Δx, the quantum uncertainty in position, could be found from the expectation values $\langle x^2\rangle$ and $\langle x\rangle$. But the argument given there applies to *any* observable, that is, the quantum uncertainty ΔQ for any observable Q is calculated as

Quantum uncertainty for any observable Q

$$\Delta Q = \sqrt{\langle Q^2\rangle - \langle Q\rangle^2} \tag{6.41}$$

Again, if $\Delta Q = 0$, Q is said to be a sharp observable and all measurements of Q yield the same value. More often, however, $\Delta Q > 0$ and repeated measurements reveal a distribution of values—as in Table 6.1 for the observable x. In such cases, we say the observable is *fuzzy*, suggesting that, prior to actual measurement, the particle cannot be said to possess a unique value of Q.

In classical physics all observables are sharp.[13] The extent to which sharp observables can be specified in quantum physics is limited by uncertainty principles, such as

$$\Delta x \, \Delta p \geq \frac{1}{2} \, \hbar \tag{6.42}$$

The uncertainties here are to be calculated from Equation 6.41. Equation 6.42 says that no matter what the state of the particle, the spread in distributions obtained in measurements of x and of p will be inversely related: when one is small, the other will be large. Alternatively, if the position of the particle is quite "fuzzy," its momentum can be relatively "sharp," and vice versa. The degree to which both may be simultaneously sharp is limited by the size of $\hbar$. The incredibly small value of $\hbar$ in SI units is an indication that quantum ideas are unnecessary at the macroscopic level.

Despite restrictions imposed by uncertainty principles, some observables in quantum physics may still be sharp. The energy E of all stationary states is one example. In the free particle plane waves of Section 6.2 we have another: The plane wave with wavenumber k,

$$\Psi_k(x, t) = e^{i(kx - \omega t)}$$

describes a particle with momentum $p = \hbar k$. Evidently, momentum is a sharp observable for this wavefunction. We find that the action of the momentum operator in this instance is especially simple:

$$[p]\Psi_k(x, t) = \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right) e^{i(kx - \omega t)} = \hbar k \Psi_k(x, t)$$

Eigenfunctions and eigenvalues

that is, the operation $[p]$ returns the original function multiplied by a constant. This is an example of an **eigenvalue problem** for the operator $[p]$.[14] The wavefunction Ψ_k is the *eigenfunction,* and the constant, in this case $\hbar k$, is the *eigenvalue*. Notice that the eigenvalue is just the sharp value of particle momentum for this wave. This connection between sharp observables and eigenvalues is a general one: **For an observable Q to be sharp, the wavefunction must be an eigenfunction of the operator for Q. Further, the sharp value for Q in this state is the eigenvalue.** In this way the eigenvalue property can serve as a simple test for sharp observables, as the following examples illustrate.

EXAMPLE 6.16   Plane Waves and Sharp Observables

Use the eigenvalue test to show that the plane wave $\Psi_k(x, t) = e^{i(kx - \omega t)}$ is one for which total energy is a sharp observable. What value does the energy take in this case?

Solution   To decide the issue we examine the action of the energy operator $[E]$ on the candidate function $e^{i(kx - \omega t)}$. Since taking a derivative with respect to t of this function is equivalent to multiplying the function by $-i\omega$, we have

$$[E]e^{i(kx - \omega t)} = \left(i\hbar \frac{\partial}{\partial t} \right) e^{i(kx - \omega t)} = \hbar \omega e^{i(kx - \omega t)}$$

---

[13]We discount in this discussion any random errors of measurement. In principle at least, the imprecision resulting from such errors can be reduced to arbitrarily low levels.

[14]The eigenvalue problem for any operator $[Q]$ is $[Q]\psi = q\psi$; that is, the result of the operation $[Q]$ on some function ψ is simply to return a multiple q of the same function. This is possible only for certain special functions ψ, the *eigenfunctions*, and then only for certain special values of q, the *eigenvalues*. Generally, $[Q]$ is known; the eigenfunctions and eigenvalues are found by imposing the eigenvalue condition.

showing that $e^{i(kx-\omega t)}$ is an eigenfunction of the energy operator $[E]$ and the eigenvalue is $\hbar\omega$. Thus, energy is a sharp observable and has the value $\hbar\omega$ in this state.

It is instructive to compare this result with the outcome found by using the other energy operator, $[H]$. The Hamiltonian for a free particle is simply the kinetic energy operator $[K]$, because the potential energy is zero in this case. Then

$$[H]e^{i(kx-\omega t)} = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right)e^{i(kx-\omega t)}$$

$$= \left(-\frac{\hbar^2}{2m}\right)(ik)^2 e^{i(kx-\omega t)}$$

Again, the operation returns the original function with a multiplier, so that $e^{i(kx-\omega t)}$ also is an eigenfunction of $[H]$. The eigenvalue in this case is $\hbar^2 k^2/2m$, which also must be the sharp value of particle energy. The equivalence with $\hbar\omega$ follows from the dispersion relation for free particles (see footnote 1).

Exercise 6   Show that total energy is a sharp observable for *any* stationary state.

EXAMPLE 6.17   Sharp Observables for a Particle in a Box

Are the stationary states of the infinite square well eigenfunctions of $[p]$? of $[p]^2$? If so, what are the eigenvalues? Discuss the implications of these results.

Solution   The candidate function in this case is any one of the square well wavefunctions $\Psi(x, t) = \sqrt{2/L}\sin(n\pi x/L)e^{-iE_n t/\hbar}$. Because the first derivative gives $(d/dx)\sin(n\pi x/L) = (n\pi/L)\cos(n\pi x/L)$, we see at once that the operator $[p]$ will *not* return the original function Ψ, and so these are not eigenfunctions of the momentum operator. They *are*, however, eigenfunctions of $[p]^2$. In particular, we have $(d^2/dx^2)\sin(n\pi x/L) = -(n\pi/L)^2\sin(n\pi x/L)$, so that

$$[p]^2\Psi(x, t) = -(\hbar/i)^2\left(\frac{n\pi}{L}\right)^2\Psi(x, t)$$

$$= \left(\frac{n\pi\hbar}{L}\right)^2\Psi(x, t)$$

The eigenvalue is the multiplier $(n\pi\hbar/L)^2$. Thus, the squared momentum (or magnitude of momentum) is sharp for such states, and repeated measurements of p^2 (or $|p|$) for the state labeled by n will give identical results equal to $(n\pi\hbar/L)^2$ (or $n\pi\hbar/L$). By contrast, the momentum itself is not sharp, meaning that different values for p will be obtained in successive measurements. In particular, it is the sign or direction of momentum that is fuzzy, consistent with the classical notion of a particle bouncing back and forth between the walls of the "box."

SUMMARY

In quantum mechanics, matter waves (or de Broglie waves) are represented by a wavefunction $\Psi(x, t)$. The probability that a particle constrained to move along the x-axis will be found in an interval dx at time t is given by $|\Psi|^2 dx$. These probabilities summed over all values of x must total 1 (certainty). That is,