

The Particle in a Box

The stationary-state wave functions and energy levels of a one-particle, one-dimensional system are found by solving the time-independent Schrödinger equation (1.19). In this chapter, we solve the time-independent Schrödinger equation for a very simple system, a particle in a one-dimensional box (Section 2.2). Because the Schrödinger equation is a differential equation, we first discuss differential equations.

2.1 Differential Equations

This section considers only **ordinary** differential equations, which are those with only one independent variable. [A **partial** differential equation has more than one independent variable. An example is the time-dependent Schrödinger equation (1.16), in which t and x are the independent variables.] An ordinary differential equation is a relation involving an independent variable x , a dependent variable $y(x)$, and the first, second, . . . , n th derivatives of y (y' , y'' , . . . , $y^{(n)}$). An example is

$$y''' + 2x(y')^2 + y^2 \sin x = 3e^x \quad (2.1)$$

The **order** of a differential equation is the order of the highest derivative in the equation. Thus, (2.1) is of third order.

A special kind of differential equation is the **linear differential equation**, which has the form

$$A_n(x)y^{(n)} + A_{n-1}(x)y^{(n-1)} + \cdots + A_1(x)y' + A_0(x)y = g(x) \quad (2.2)$$

where the A 's and g (some of which may be zero) are functions of x only. In the n th-order linear differential equation (2.2), y and its derivatives appear to the first power. A differential equation that cannot be put in the form (2.2) is **nonlinear**. If $g(x) = 0$ in (2.2), the linear differential equation is **homogeneous**; otherwise it is **inhomogeneous**. The one-dimensional Schrödinger equation (1.19) is a linear homogeneous second-order differential equation.

By dividing by the coefficient of y'' , we can put every linear homogeneous second-order differential equation into the form

$$y'' + P(x)y' + Q(x)y = 0 \quad (2.3)$$

Suppose y_1 and y_2 are two independent functions, each of which satisfies (2.3). By independent, we mean that y_2 is not simply a multiple of y_1 . Then the general solution of the linear homogeneous differential equation (2.3) is

$$y = c_1y_1 + c_2y_2 \quad (2.4)$$

where c_1 and c_2 are arbitrary constants. This is readily verified by substituting (2.4) into the left side of (2.3):

$$\begin{aligned} c_1 y_1'' + c_2 y_2'' + P(x)c_1 y_1' + P(x)c_2 y_2' + Q(x)c_1 y_1 + Q(x)c_2 y_2 \\ = c_1 [y_1'' + P(x)y_1' + Q(x)y_1] + c_2 [y_2'' + P(x)y_2' + Q(x)y_2] \\ = c_1 \cdot 0 + c_2 \cdot 0 = 0 \end{aligned} \quad (2.5)$$

where the fact that y_1 and y_2 satisfy (2.3) has been used.

The general solution of a differential equation of n th order usually has n arbitrary constants. To fix these constants, we may have **boundary conditions**, which are conditions that specify the value of y or various of its derivatives at a point or points. For example, if y is the displacement of a vibrating string held fixed at two points, we know y must be zero at these points.

An important special case is a linear homogeneous second-order differential equation with **constant coefficients**:

$$y'' + py' + qy = 0 \quad (2.6)$$

where p and q are constants. To solve (2.6), let us tentatively assume a solution of the form $y = e^{sx}$. We are looking for a function whose derivatives when multiplied by constants will cancel the original function. The exponential function repeats itself when differentiated and is thus the correct choice. Substitution in (2.6) gives

$$s^2 e^{sx} + p s e^{sx} + q e^{sx} = 0$$

$$s^2 + ps + q = 0 \quad (2.7)$$

Equation (2.7) is called the **auxiliary equation**. It is a quadratic equation with two roots s_1 and s_2 that, provided s_1 and s_2 are not equal, give two independent solutions to (2.6). Thus, the general solution of (2.6) is

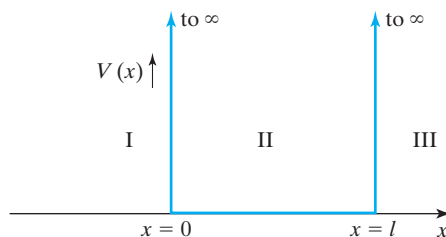
$$y = c_1 e^{s_1 x} + c_2 e^{s_2 x} \quad (2.8)$$

For example, for $y'' + 6y' - 7y = 0$, the auxiliary equation is $s^2 + 6s - 7 = 0$. The quadratic formula gives $s_1 = 1$, $s_2 = -7$, so the general solution is $c_1 e^x + c_2 e^{-7x}$.

2.2 Particle in a One-Dimensional Box

This section solves the time-independent Schrödinger equation for a particle in a one-dimensional box. By this we mean a particle subjected to a potential-energy function that is infinite everywhere along the x axis except for a line segment of length l , where the potential energy is zero. Such a system may seem physically unreal, but this model can be applied with some success to certain conjugated molecules; see Prob. 2.17. We put the origin at the left end of the line segment (Fig. 2.1).

FIGURE 2.1 Potential energy function $V(x)$ for the particle in a one-dimensional box.



We have three regions to consider. In regions I and III, the potential energy V equals infinity and the time-independent Schrödinger equation (1.19) is

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

Neglecting E in comparison with ∞ , we have

$$\frac{d^2\psi}{dx^2} = \infty\psi, \quad \psi = \frac{1}{\infty} \frac{d^2\psi}{dx^2}$$

and we conclude that ψ is zero outside the box:

$$\psi_I = 0, \quad \psi_{III} = 0 \quad (2.9)$$

For region II, x between zero and l , the potential energy V is zero, and the Schrödinger equation (1.19) becomes

$$\frac{d^2\psi_{II}}{dx^2} + \frac{2m}{\hbar^2} E\psi_{II} = 0 \quad (2.10)$$

where m is the mass of the particle and E is its energy. We recognize (2.10) as a linear homogeneous second-order differential equation with constant coefficients. The auxiliary equation (2.7) gives

$$s^2 + 2mE\hbar^{-2} = 0$$

$$s = \pm (-2mE)^{1/2}\hbar^{-1} \quad (2.11)$$

$$s = \pm i(2mE)^{1/2}/\hbar \quad (2.12)$$

where $i = \sqrt{-1}$. Using (2.8), we have

$$\psi_{II} = c_1 e^{i(2mE)^{1/2}x/\hbar} + c_2 e^{-i(2mE)^{1/2}x/\hbar} \quad (2.13)$$

Temporarily, let

$$\theta \equiv (2mE)^{1/2}x/\hbar$$

$$\psi_{II} = c_1 e^{i\theta} + c_2 e^{-i\theta}$$

We have $e^{i\theta} = \cos \theta + i \sin \theta$ [Eq. (1.28)] and $e^{-i\theta} = \cos(-\theta) + i \sin(-\theta) = \cos \theta - i \sin \theta$, since

$\cos(-\theta) = \cos \theta \quad \text{and} \quad \sin(-\theta) = -\sin \theta$

(2.14)

Therefore,

$$\begin{aligned} \psi_{II} &= c_1 \cos \theta + ic_1 \sin \theta + c_2 \cos \theta - ic_2 \sin \theta \\ &= (c_1 + c_2) \cos \theta + (ic_1 - ic_2) \sin \theta \\ &= A \cos \theta + B \sin \theta \end{aligned}$$

where A and B are new arbitrary constants. Hence,

$$\psi_{II} = A \cos[\hbar^{-1}(2mE)^{1/2}x] + B \sin[\hbar^{-1}(2mE)^{1/2}x] \quad (2.15)$$

Now we find A and B by applying boundary conditions. It seems reasonable to postulate that the wave function will be continuous; that is, it will make no sudden jumps in

value (see Fig. 3.4). If ψ is to be continuous at the point $x = 0$, then ψ_I and ψ_{II} must approach the same value at $x = 0$:

$$\begin{aligned}\lim_{x \rightarrow 0} \psi_I &= \lim_{x \rightarrow 0} \psi_{II} \\ 0 &= \lim_{x \rightarrow 0} \{ A \cos[\hbar^{-1}(2mE)^{1/2}x] + B \sin[\hbar^{-1}(2mE)^{1/2}x] \} \\ 0 &= A\end{aligned}$$

since

$$\sin 0 = 0 \quad \text{and} \quad \cos 0 = 1 \quad (2.16)$$

With $A = 0$, Eq. (2.15) becomes

$$\psi_{II} = B \sin[(2\pi/h)(2mE)^{1/2}x] \quad (2.17)$$

Applying the continuity condition at $x = l$, we get

$$B \sin[(2\pi/h)(2mE)^{1/2}l] = 0 \quad (2.18)$$

B cannot be zero because this would make the wave function zero everywhere—we would have an empty box. Therefore,

$$\sin[(2\pi/h)(2mE)^{1/2}l] = 0$$

The zeros of the sine function occur at $0, \pm\pi, \pm2\pi, \pm3\pi, \dots = \pm n\pi$. Hence,

$$(2\pi/h)(2mE)^{1/2}l = \pm n\pi \quad (2.19)$$

The value $n = 0$ is a special case. From (2.19), $n = 0$ corresponds to $E = 0$. For $E = 0$, the roots (2.12) of the auxiliary equation are equal and (2.13) is not the complete solution of the Schrödinger equation. To find the complete solution, we return to (2.10), which for $E = 0$ reads $d^2\psi_{II}/dx^2 = 0$. Integration gives $d\psi_{II}/dx = c$ and $\psi_{II} = cx + d$, where c and d are constants. The boundary condition that $\psi_{II} = 0$ at $x = 0$ gives $d = 0$, and the condition that $\psi_{II} = 0$ at $x = l$ then gives $c = 0$. Thus, $\psi_{II} = 0$ for $E = 0$, and therefore $E = 0$ is not an allowed energy value. Hence, $n = 0$ is not allowed.

Solving (2.19) for E , we have

$$E = \frac{n^2 h^2}{8ml^2} \quad n = 1, 2, 3, \dots \quad (2.20)$$

Only the energy values (2.20) allow ψ to satisfy the boundary condition of continuity at $x = l$. Application of a boundary condition has forced us to the conclusion that the values of the energy are quantized (Fig. 2.2). This is in striking contrast to the classical result that the particle in the box can have any nonnegative energy. Note that there is a minimum value, greater than zero, for the energy of the particle. The state of lowest energy is called the **ground state**. States with energies higher than the ground-state energy are **excited states**. (In classical mechanics, the lowest possible energy of a particle in a box is zero. The classical particle sits motionless inside the box with zero kinetic energy and zero potential energy.)

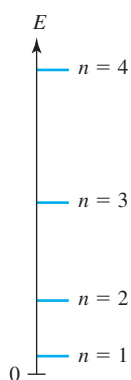


FIGURE 2.2 Lowest four energy levels for the particle in a one-dimensional box.

EXAMPLE

A particle of mass 2.00×10^{-26} g is in a one-dimensional box of length 4.00 nm. Find the frequency and wavelength of the photon emitted when this particle goes from the $n = 3$ to the $n = 2$ level.

By conservation of energy, the energy $h\nu$ of the emitted photon equals the energy difference between the two stationary states [Eq. (1.4); see also Section 9.9]:

$$h\nu = E_{\text{upper}} - E_{\text{lower}} = \frac{n_u^2 h^2}{8ml^2} - \frac{n_l^2 h^2}{8ml^2}$$

$$\nu = \frac{(n_u^2 - n_l^2)h}{8ml^2} = \frac{(3^2 - 2^2)(6.626 \times 10^{-34} \text{ J s})}{8(2.00 \times 10^{-29} \text{ kg})(4.00 \times 10^{-9} \text{ m})^2} = 1.29 \times 10^{12} \text{ s}^{-1}$$

where u and l stand for upper and lower. Use of $\lambda\nu = c$ gives $\lambda = 2.32 \times 10^{-4} \text{ m}$. (A common student error is to set $h\nu$ equal to the energy of one of the states instead of the energy *difference* between states.)

EXERCISE For an electron in a certain one-dimensional box, the longest-wavelength transition occurs at 400 nm. Find the length of the box. (*Answer:* 0.603 nm.)

Substitution of (2.19) into (2.17) gives for the wave function

$$\psi_{\text{II}} = B \sin\left(\frac{n\pi x}{l}\right), \quad n = 1, 2, 3, \dots \quad (2.21)$$

The use of the negative sign in front of $n\pi$ does not give us another independent solution. Since $\sin(-\theta) = -\sin \theta$, we would simply get a constant, -1 , times the solution with the plus sign.

The constant B in Eq. (2.21) is still arbitrary. To fix its value, we use the normalization requirement, Eqs. (1.24) and (1.22):

$$\int_{-\infty}^{\infty} |\Psi|^2 dx = \int_{-\infty}^{\infty} |\psi|^2 dx = 1$$

$$\int_{-\infty}^0 |\psi_{\text{I}}|^2 dx + \int_0^l |\psi_{\text{II}}|^2 dx + \int_l^{\infty} |\psi_{\text{III}}|^2 dx = 1$$

$$|B|^2 \int_0^l \sin^2\left(\frac{n\pi x}{l}\right) dx = 1 = |B|^2 \frac{l}{2} \quad (2.22)$$

where the integral was evaluated by using Eq. (A.2) in the Appendix. We have

$$|B| = (2/l)^{1/2}$$

Note that only the absolute value of B has been found. B could be $-(2/l)^{1/2}$ as well as $(2/l)^{1/2}$. Moreover, B need not be a real number. We could use any complex number with absolute value $(2/l)^{1/2}$. All we can say is that $B = (2/l)^{1/2} e^{i\alpha}$, where α is the phase of B and could be any value in the range 0 to 2π (Section 1.7). Choosing the phase to be zero, we write as the stationary-state wave functions for the particle in a box

$$\psi_{\text{II}} = \left(\frac{2}{l}\right)^{1/2} \sin\left(\frac{n\pi x}{l}\right), \quad n = 1, 2, 3, \dots \quad (2.23)$$

Graphs of the wave functions and the probability densities are shown in **Figs. 2.3** and **2.4**.

The number n in the energies (2.20) and the wave functions (2.23) is called a **quantum number**. Each different value of the quantum number n gives a different wave function and a different state.

FIGURE 2.3 Graphs of ψ for the three lowest-energy particle-in-a-box states.

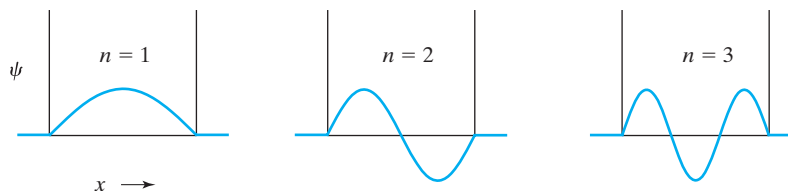
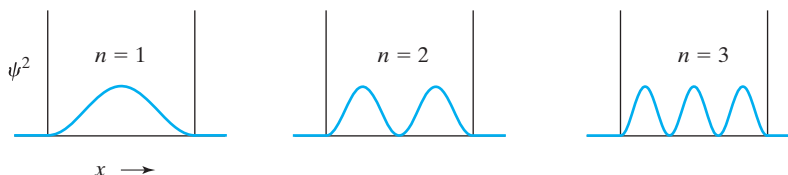


FIGURE 2.4 Graphs of $|\psi|^2$ for the lowest particle-in-a-box states.



The wave function is zero at certain points; these points are called **nodes**. For each increase of one in the value of the quantum number n , ψ has one more node. The existence of nodes in ψ and $|\psi|^2$ may seem surprising. Thus, for $n = 2$, Fig. 2.4 says that there is zero probability of finding the particle in the center of the box at $x = l/2$. How can the particle get from one side of the box to the other without at any time being found in the center? This apparent paradox arises from trying to understand the motion of microscopic particles using our everyday experience of the motions of macroscopic particles. However, as noted in Chapter 1, electrons and other microscopic “particles” cannot be fully and correctly described in terms of concepts of classical physics drawn from the macroscopic world.

Figure 2.4 shows that the probability of finding the particle at various places in the box is quite different from the classical result. Classically, a particle of fixed energy in a box bounces back and forth elastically between the two walls, moving at constant speed. Thus it is equally likely to be found at any point in the box. Quantum mechanically, we find a maximum in probability at the center of the box for the lowest energy level. As we go to higher energy levels with more nodes, the maxima and minima of probability come closer together, and the variations in probability along the length of the box ultimately become undetectable. For very high quantum numbers, we approach the classical result of uniform probability density.

This result, that in the limit of large quantum numbers quantum mechanics goes over into classical mechanics, is known as the *Bohr correspondence principle*. Since Newtonian mechanics holds for macroscopic bodies (moving at speeds much less than the speed of light), we expect nonrelativistic quantum mechanics to give the same answer as classical mechanics for macroscopic bodies. Because of the extremely small size of Planck’s constant, quantization of energy is unobservable for macroscopic bodies. Since the mass of the particle and the length of the box squared appear in the denominator of Eq. (2.20), a macroscopic object in a macroscopic box having a macroscopic energy of motion would have a huge value for n , and hence, according to the correspondence principle, would show classical behavior.

We have a whole set of wave functions, each corresponding to a different energy and characterized by the quantum number n , which is a positive integer. Let the subscript i denote a particular wave function with the value n_i for its quantum number:

$$\psi_i = \left(\frac{2}{l}\right)^{1/2} \sin\left(\frac{n_i \pi x}{l}\right), \quad 0 < x < l$$

$$\psi_i = 0 \quad \text{elsewhere}$$

Since the wave function has been normalized, we have

$$\int_{-\infty}^{\infty} \psi_i^* \psi_j dx = 1 \quad \text{if } i = j \quad (2.24)$$

We now ask for the value of this integral when we use wave functions corresponding to *different* energy levels:

$$\int_{-\infty}^{\infty} \psi_i^* \psi_j dx = \int_0^l \left(\frac{2}{l}\right)^{1/2} \sin\left(\frac{n_i \pi x}{l}\right) \left(\frac{2}{l}\right)^{1/2} \sin\left(\frac{n_j \pi x}{l}\right) dx, \quad n_i \neq n_j$$

Use of Eq. (A.5) in the Appendix gives

$$\int_{-\infty}^{\infty} \psi_i^* \psi_j dx = \frac{2}{l} \left[\frac{\sin[(n_i - n_j)\pi]}{2(n_i - n_j)\pi/l} - \frac{\sin[(n_i + n_j)\pi]}{2(n_i + n_j)\pi/l} \right] = 0 \quad (2.25)$$

since $\sin m\pi = 0$ for m an integer. We thus have

$$\int_{-\infty}^{\infty} \psi_i^* \psi_j dx = 0, \quad i \neq j \quad (2.26)$$

When (2.26) holds, the functions ψ_i and ψ_j are said to be **orthogonal** to each other for $i \neq j$. We can combine (2.24) and (2.26) by writing

$$\int_{-\infty}^{\infty} \psi_i^* \psi_j dx = \delta_{ij} \quad (2.27)$$

The symbol δ_{ij} is called the **Kronecker delta** (after a mathematician). It equals 1 when the two indexes i and j are equal, and it equals 0 when i and j are unequal:

$$\delta_{ij} \equiv \begin{cases} 0 & \text{for } i \neq j \\ 1 & \text{for } i = j \end{cases} \quad (2.28)$$

The property (2.27) of the wave functions is called **orthonormality**. We proved orthonormality only for the particle-in-a-box wave functions. We shall prove it more generally in Section 7.2.

You might be puzzled by Eq. (2.26) and wonder why we would want to multiply the wave function of one state by the wave function of a different state. We will later see (Section 7.3, for example) that it is often helpful to use equations that contain a sum involving all the wave functions of a system, and such equations can lead to integrals like that in (2.26).

A more rigorous way to look at the particle in a box with infinite walls is to first treat the particle in a box with a finite jump in potential energy at the walls and then take the limit as the jump in V becomes infinite. The results, when the limit is taken, will be the same as (2.20) and (2.23) (see Prob. 2.22).

We have considered only the stationary states of the particle in a one-dimensional box. For an example of a nonstationary state of this system, see the example near the end of Section 7.8.

Some online computer simulations of the particle in a box can be found at www.chem.uci.edu/undergraduate/applets/dwell/dwell.htm (shows the effects on the wave functions and energy levels when a barrier of variable height and width is introduced into the middle of the box); web.williams.edu/wp-etc/chemistry/dbingemann/Chem153/particle.html (shows quantization by plotting the solution to the Schrödinger equation as the energy is varied and as the box length is varied); and falstad.com/qm1d/ (shows both time-independent and time-dependent states; see Prob. 7.47).

2.3 The Free Particle in One Dimension

By a free particle, we mean a particle subject to no forces whatever. For a free particle, integration of (1.12) shows that the potential energy remains constant no matter what the value of x is. Since the choice of the zero level of energy is arbitrary, we may set $V(x) = 0$. The Schrödinger equation (1.19) becomes

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} E\psi = 0 \quad (2.29)$$

Equation (2.29) is the same as Eq. (2.10) (except for the boundary conditions). Therefore, the general solution of (2.29) is (2.13):

$$\psi = c_1 e^{i(2mE)^{1/2}x/\hbar} + c_2 e^{-i(2mE)^{1/2}x/\hbar} \quad (2.30)$$

What boundary condition might we impose? It seems reasonable to postulate (since $\psi^*\psi dx$ represents a probability) that ψ will remain finite as x goes to $\pm\infty$. If the energy E is less than zero, then this boundary condition will be violated, since for $E < 0$ we have

$$i(2mE)^{1/2} = i(-2m|E|)^{1/2} = i \cdot i \cdot (2m|E|)^{1/2} = -(2m|E|)^{1/2}$$

and therefore the first term in (2.30) will become infinite as x approaches minus infinity. Similarly, if E is negative, the second term in (2.30) becomes infinite as x approaches plus infinity. Thus the boundary condition requires

$$E \geq 0 \quad (2.31)$$

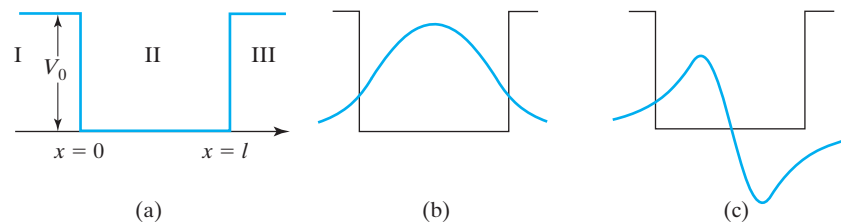
for the free particle. The wave function is oscillatory and is a linear combination of a sine and a cosine term [Eq. (2.15)]. For the free particle, the energy is not quantized; all non-negative energies are allowed. Since we set $V = 0$, the energy E is in this case all kinetic energy. If we try to evaluate the arbitrary constants c_1 and c_2 by normalization, we will find that the integral $\int_{-\infty}^{\infty} \psi^*(x)\psi(x) dx$ is infinite. In other words, the free-particle wave function is not normalizable in the usual sense. This is to be expected on physical grounds because there is no reason for the probability of finding the free particle to approach zero as x goes to $\pm\infty$.

The free-particle problem is an unreal situation because we could not actually have a particle that had no interaction with any other particle in the universe.

2.4 Particle in a Rectangular Well

Consider a particle in a one-dimensional box with walls of finite height (Fig. 2.5a). The potential-energy function is $V = V_0$ for $x < 0$, $V = 0$ for $0 \leq x \leq l$, and $V = V_0$ for $x > l$. There are two cases to examine, depending on whether the particle's energy E is less than or greater than V_0 .

FIGURE 2.5 (a) Potential energy for a particle in a one-dimensional rectangular well. (b) The ground-state wave function for this potential. (c) The first excited-state wave function.



We first consider $E < V_0$. The Schrödinger equation (1.19) in regions I and III is $d^2\psi/dx^2 + (2m/\hbar^2)(E - V_0)\psi = 0$. This is a linear homogeneous differential equation with constant coefficients, and the auxiliary equation (2.7) is $s^2 + (2m/\hbar^2)(E - V_0) = 0$ with roots $s = \pm (2m/\hbar^2)^{1/2}(V_0 - E)^{1/2}$. Therefore,

$$\begin{aligned}\psi_I &= C \exp[(2m/\hbar^2)^{1/2}(V_0 - E)^{1/2}x] + D \exp[-(2m/\hbar^2)^{1/2}(V_0 - E)^{1/2}x] \\ \psi_{III} &= F \exp[(2m/\hbar^2)^{1/2}(V_0 - E)^{1/2}x] + G \exp[-(2m/\hbar^2)^{1/2}(V_0 - E)^{1/2}x]\end{aligned}$$

where C , D , F , and G are constants.

As in Section 2.3, we must prevent ψ_I from becoming infinite as $x \rightarrow -\infty$. Since we are assuming $E < V_0$, the quantity $(V_0 - E)^{1/2}$ is a real, positive number, and to keep ψ_I finite as $x \rightarrow -\infty$, we must have $D = 0$. Similarly, to keep ψ_{III} finite as $x \rightarrow +\infty$, we must have $F = 0$. Therefore,

$$\psi_I = C \exp[(2m/\hbar^2)^{1/2}(V_0 - E)^{1/2}x], \quad \psi_{III} = G \exp[-(2m/\hbar^2)^{1/2}(V_0 - E)^{1/2}x]$$

In region II, $V = 0$, the Schrödinger equation is (2.10) and its solution is (2.15):

$$\psi_{II} = A \cos[(2m/\hbar^2)^{1/2}E^{1/2}x] + B \sin[(2m/\hbar^2)^{1/2}E^{1/2}x] \quad (2.32)$$

To complete the problem, we must apply the boundary conditions. As with the particle in a box with infinite walls, we require the wave function to be continuous at $x = 0$ and at $x = l$; so $\psi_I(0) = \psi_{II}(0)$ and $\psi_{II}(l) = \psi_{III}(l)$. The wave function has four arbitrary constants, so more than these two boundary conditions are needed. As well as requiring ψ to be continuous, we shall require that its derivative $d\psi/dx$ be continuous everywhere. To justify this requirement, we note that if $d\psi/dx$ changed discontinuously at a point, then its derivative (its instantaneous rate of change) $d^2\psi/dx^2$ would become infinite at that point. However, for the particle in a rectangular well, the Schrödinger equation $d^2\psi/dx^2 = (2m/\hbar^2)(V - E)\psi$ does not contain anything infinite on the right side, so $d^2\psi/dx^2$ cannot become infinite. [For a more rigorous argument, see D. Branson, *Am. J. Phys.*, **47**, 1000 (1979).] Therefore, $d\psi_I/dx = d\psi_{II}/dx$ at $x = 0$ and $d\psi_{II}/dx = d\psi_{III}/dx$ at $x = l$.

From $\psi_I(0) = \psi_{II}(0)$, we get $C = A$. From $\psi'_I(0) = \psi'_{II}(0)$, we get (Prob. 2.21a) $B = (V_0 - E)^{1/2}A/E^{1/2}$. From $\psi_{II}(l) = \psi_{III}(l)$, we get a complicated equation that allows G to be found in terms of A . The constant A is found by normalization.

Taking $\psi'_{II}(l) = \psi'_{III}(l)$, dividing it by $\psi_{II}(l) = \psi_{III}(l)$, and expressing B in terms of A , we get the following equation for the energy levels (Prob. 2.21b):

$$(2E - V_0) \sin[(2mE)^{1/2}l/\hbar] = 2(V_0E - E^2)^{1/2} \cos[(2mE)^{1/2}l/\hbar] \quad (2.33)$$

[Although $E = 0$ satisfies (2.33), it is not an allowed energy value, since it gives $\psi = 0$ (Prob. 2.30).] Defining the dimensionless constants ε and b as

$$\varepsilon \equiv E/V_0 \quad \text{and} \quad b \equiv (2mV_0)^{1/2}l/\hbar \quad (2.34)$$

we divide (2.33) by V_0 to get

$$(2\varepsilon - 1) \sin(b\varepsilon^{1/2}) - 2(\varepsilon - \varepsilon^2)^{1/2} \cos(b\varepsilon^{1/2}) = 0 \quad (2.35)$$

Only the particular values of E that satisfy (2.33) give a wave function that is continuous and has a continuous derivative, so the energy levels are quantized for $E < V_0$. To find the allowed energy levels, we can plot the left side of (2.35) versus ε for $0 < \varepsilon < 1$ and find the points where the curve crosses the horizontal axis (see also Prob. 4.31c). A detailed study (Merzbacher, Section 6.8) shows that the number of allowed energy levels with $E < V_0$ is N , where N satisfies

$$N - 1 < b/\pi \leq N, \quad \text{where } b \equiv (2mV_0)^{1/2}l/\hbar \quad (2.36)$$

For example, if $V_0 = \hbar^2/ml^2$, then $b/\pi = 2(2^{1/2}) = 2.83$, and $N = 3$.

Figure 2.5 shows ψ for the lowest two energy levels. The wave function is oscillatory inside the box and dies off exponentially outside the box. It turns out that the number of nodes increases by one for each higher level.

So far we have considered only states with $E < V_0$. For $E > V_0$, the quantity $(V_0 - E)^{1/2}$ is imaginary, and instead of dying off to zero as x goes to $\pm \infty$, ψ_I and ψ_{III} oscillate (similar to the free-particle ψ). We no longer have any reason to set D in ψ_I and F in ψ_{III} equal to zero, and with these additional constants available to satisfy the boundary conditions on ψ and ψ' , one finds that E need not be restricted to obtain properly behaved wave functions. Therefore, all energies above V_0 are allowed.

A state in which $\psi \rightarrow 0$ as $x \rightarrow \infty$ and as $x \rightarrow -\infty$ is called a **bound state**. For a bound state, significant probability for finding the particle exists in only a finite region of space. For an **unbound state**, ψ does not go to zero as $x \rightarrow \pm \infty$ and is not normalizable. For the particle in a rectangular well, states with $E < V_0$ are bound and states with $E > V_0$ are unbound. For the particle in a box with infinitely high walls, all states are bound. For the free particle, all states are unbound.

For an online simulation of the particle in a well, go to www.falstad.com/qm1d and choose Finite Well in the Setup box. You can vary the well width and depth and see the effect on the energy levels and wave functions.

2.5 Tunneling

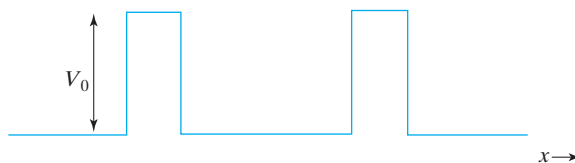
For the particle in a rectangular well (Section 2.4), Fig. 2.5 and the equations for ψ_I and ψ_{III} show that for the bound states there is a nonzero probability of finding the particle in regions I and III, where its total energy E is less than its potential energy $V = V_0$. Classically, this behavior is not allowed. The classical equations $E = T + V$ and $T \geq 0$, where T is the kinetic energy, mean that E cannot be less than V in classical mechanics.

Consider a particle in a one-dimensional box with walls of finite height and finite thickness (Fig. 2.6). Classically, the particle cannot escape from the box unless its energy is greater than the potential-energy barrier V_0 . However, a quantum-mechanical treatment (which is omitted) shows that there is a finite probability for a particle of total energy less than V_0 to be found outside the box.

The term **tunneling** denotes the penetration of a particle into a classically forbidden region (as in Fig. 2.5) or the passage of a particle through a potential-energy barrier whose height exceeds the particle's energy. Since tunneling is a quantum effect, its probability of occurrence is greater the less classical is the behavior of the particle. Therefore, tunneling is most prevalent with particles of small mass. (Note that the greater the mass m , the more rapidly the functions ψ_I and ψ_{III} of Section 2.4 die away to zero.) Electrons tunnel quite readily. Hydrogen atoms and ions tunnel more readily than heavier atoms.

The emission of alpha particles from a radioactive nucleus involves tunneling of the alpha particles through the potential-energy barrier produced by the short-range attractive nuclear forces and the Coulombic repulsive force between the daughter nucleus and the alpha particle. The NH_3 molecule is pyramidal. There is a potential-energy barrier to inversion of the molecule, with the potential-energy maximum occurring at the planar configuration. The hydrogen atoms can tunnel through this barrier, thereby inverting the molecule. In CH_3CH_3 there is a barrier to internal rotation, with a potential-energy

FIGURE 2.6 Potential energy for a particle in a one-dimensional box of finite height and thickness.



maximum at the eclipsed position of the hydrogens. The hydrogens can tunnel through this barrier from one staggered position to the next. Tunneling of electrons is important in oxidation–reduction reactions and in electrode processes. Tunneling usually contributes significantly to the rate of chemical reactions that involve transfer of hydrogen atoms. See R. P. Bell, *The Tunnel Effect in Chemistry*, Chapman & Hall, 1980.

Tunneling of H atoms occurs in some enzyme-catalyzed reactions; see *Quantum Tunnelling in Enzyme-Catalyzed Reactions*, R. Allemann and N. Scrutton (eds.), RSC Publishing, 2009.

The scanning tunneling microscope, invented in 1981, uses the tunneling of electrons through the space between the extremely fine tip of a metal wire and the surface of an electrically conducting solid to produce images of individual atoms on the solid's surface. A small voltage is applied between the solid and the wire, and as the tip is moved across the surface at a height of a few angstroms, the tip height is adjusted to keep the current flow constant. A plot of tip height versus position gives an image of the surface.

Summary

The general solution to the linear, homogeneous, second-order, constant-coefficients differential equation $y''(x) + py'(x) + qy(x) = 0$ is $y = c_1e^{s_1x} + c_2e^{s_2x}$, where s_1 and s_2 are the solutions to the auxiliary equation $s^2 + ps + q = 0$.

For a particle in a one-dimensional box (potential energy $V = 0$ for $0 \leq x \leq l$ and $V = \infty$ elsewhere), the stationary-state wave functions and energies are $\psi = (2/l)^{1/2} \sin(n\pi x/l)$ for $0 \leq x \leq l$, $\psi = 0$ elsewhere, and $E = n^2h^2/8ml^2$, where $n = 1, 2, 3, \dots$. The number of nodes (places where $\psi = 0$) increases by 1 for each increase of 1 in the quantum number n . The wave functions are orthonormal [Eq. (2.27)].

For a free particle ($V = 0$ everywhere), all nonnegative energies are allowed, and the wave function is not normalizable in the usual sense.

The particle in a rectangular one-dimensional well with walls of finite height has a finite number of bound states [Eq. (2.36)]. The bound-state wave functions are oscillatory inside the well and die off exponentially to zero outside the well. The energies of the unbound states are not quantized.

Tunneling is the penetration of a particle into a classically forbidden region or the passage of a particle through a potential-energy barrier whose height is greater than the particle's energy.

Problems

Sec.	2.1	2.2	2.3	2.4	general
Probs.	2.1–2.4	2.5–2.19	2.20	2.21–2.30	2.31–2.32

- 2.1** (a) Solve $y''(x) + y'(x) - 6y(x) = 0$. (b) Evaluate the arbitrary constants in the solution if the boundary conditions are $y = 0$ at $x = 0$ and $y' = 1$ at $x = 0$.
- 2.2** If $y = c_1e^{(2+i)x} + c_2e^{(2-i)x}$, where c_1 and c_2 are constants, find the second-order, linear homogeneous differential equation with constant coefficients that y satisfies.
- 2.3** (a) For the case of equal roots of the auxiliary equation, $s_1 = s_2 = s$, we have found only one independent solution of the linear homogeneous second-order differential equation: e^{sx} . Verify that xe^{sx} is the second solution in this case. (b) Solve $y''(x) - 2y'(x) + y(x) = 0$.
- 2.4** For each of these choices of F in Newton's second law (1.8), classify (1.8) as a linear or nonlinear differential equation (a , b , c , and k are constants). (a) $F = c$; (b) $F = -kx$; (c) $F = -ax^3$; (d) $F = b \sin ax$; (e) $F = a - kx$. [Classical-mechanical systems that show chaotic behavior (Section 1.4) obey nonlinear differential equations, but not all nonlinear differential equations give rise to chaotic behavior.]

- 2.5** True or false? (a) The ground-state energy of a particle in a box (PIB) is zero. (b) The PIB energy levels are equally spaced. (c) Increasing PIB stationary-state energy corresponds to increasing number of nodes in the wave function. (d) Every solution of the PIB time-independent Schrödinger equation is an allowed stationary-state wave function. (e) The PIB transition that absorbs the photon of longest wavelength is from the $n = 1$ level to the $n = 2$ level.
- 2.6** For a particle in a one-dimensional box of length l , consider an infinitesimal interval of length dl that lies within the box. For each of the following stationary states, state which location(s) of this interval gives a maximum probability and which gives a minimum probability to find the particle in the interval. (a) $n = 1$; (b) $n = 2$; (c) $n = 3$.
- 2.7** Consider a particle with quantum number n moving in a one-dimensional box of length l . (a) Find the probability of finding the particle in the left quarter of the box. (b) For what value of n is this probability a maximum? (c) What is the limit of this probability for $n \rightarrow \infty$? (d) What principle is illustrated in (c)?
- 2.8** Consider an electron in a one-dimensional box of length $2.000 \text{ \AA}$ with the left end of the box at $x = 0$. (a) Suppose we have one million of these systems, each in the $n = 1$ state, and we measure the x coordinate of the electron in each system. About how many times will the electron be found between $0.600 \text{ \AA}$ and $0.601 \text{ \AA}$? Consider the interval to be infinitesimal. *Hint:* Check whether your calculator is set to degrees or radians. (b) Suppose we have a large number of these systems, each in the $n = 1$ state, and we measure the x coordinate of the electron in each system and find the electron between $0.700 \text{ \AA}$ and $0.701 \text{ \AA}$ in 126 of the measurements. In about how many measurements will the electron be found between $1.000 \text{ \AA}$ and $1.001 \text{ \AA}$?
- 2.9** (a) Sketch rough graphs of ψ and of ψ^2 for the $n = 4$ and $n = 5$ particle-in-a-box states. (b) Use calculus to find the slope of the ψ^2 curve for $n = 4$ at $x = \frac{1}{2}l$ and check that your curve was drawn with the correct slope.
- 2.10** An extremely crude picture of a valence electron in an atom or a molecule treats it as a particle in a one-dimensional box whose length is on the order of the size of atoms and molecules. (a) For an electron in a one-dimensional box of length $1.0 \text{ \AA}$, calculate the separation between the two lowest energy levels. (b) Calculate the wavelength of a photon corresponding to a transition between these two levels. (c) In what portion of the electromagnetic spectrum is this wavelength?
- 2.11** For a macroscopic object of mass 1.0 g moving with speed 1.0 cm/s in a one-dimensional box of length 1.0 cm , find the quantum number n .
- 2.12** When a particle of mass $9.1 \times 10^{-28} \text{ g}$ in a certain one-dimensional box goes from the $n = 5$ level to the $n = 2$ level, it emits a photon of frequency $6.0 \times 10^{14} \text{ s}^{-1}$. Find the length of the box.
- 2.13** When an electron in a certain excited energy level in a one-dimensional box of length $2.00 \text{ \AA}$ makes a transition to the ground state, a photon of wavelength 8.79 nm is emitted. Find the quantum number of the initial state.
- 2.14** The $n = 1$ to $n = 2$ absorption frequency for a certain particle in a certain one-dimensional box is $6.0 \times 10^{12} \text{ s}^{-1}$. Find the $n = 2$ to $n = 3$ absorption frequency for this system.
- 2.15** An electron in a stationary state of a one-dimensional box of length 0.300 nm emits a photon of frequency $5.05 \times 10^{15} \text{ s}^{-1}$. Find the initial and final quantum numbers for this transition.
- 2.16** We will see in Section 9.9 that when a charged particle in a one-dimensional box (PIB) absorbs or emits a photon, the quantum number n must change by an odd integer: $\Delta n = \pm 1, \pm 3, \pm 5, \dots$. Transitions with n changing by an even integer are not allowed for the PIB. Show that the allowed transition frequencies have the form $\nu = k(h/8ml^2)$, where k takes on certain whole-number values. Find the smallest value of k for which two different Δn values give the same emission frequency. *Hint:* First examine the pattern of transition frequencies for which n changes by 1 and the lower-level n value is 1 or 2 or 3 or $\dots$; then consider n changing by 3 with the lower level being 1 or 2 or 3 or $\dots$.
- 2.17** A crude treatment of the π electrons of a conjugated molecule regards these electrons as moving in the particle-in-a-box potential of Fig. 2.1, where the box length is somewhat more than the length of the conjugated chain. The Pauli exclusion principle (Chapter 10) allows no more than two electrons to occupy each box level. (These two have opposite spins.) For 1,3-butadiene, $\text{CH}_2=\text{CHCH}=\text{CH}_2$, take the box length as $7.0 \text{ \AA}$ and use this model to estimate the wavelength

of light absorbed when a π electron is excited from the highest-occupied to the lowest-vacant box level of the molecular electronic ground state. The experimental value is 217 nm.

- 2.18 For the particle in a one-dimensional box of length l , we could have put the coordinate origin at the center of the box. Find the wave functions and energy levels for this choice of origin.
- 2.19 The particle-in-a-box time-independent Schrödinger equation contains the constants h and m , and the boundary conditions involve the box length l . We therefore expect the stationary-state energies to be a function of h , m , and l ; that is, $E = f(h, m, l)$. [We found $E = (n^2/8)(h^2/ml^2)$.] Prove that the only values of a , b , and c that give the product $h^a m^b l^c$ the dimensions of energy are $a = 2$, $b = -1$, $c = -2$.
- 2.20 Write down the time-dependent wave function for a free particle with energy E .
- 2.21 (a) For the particle in a rectangular well (Section 2.4), verify that $B = (V_0 - E)^{1/2} A/E^{1/2}$. (b) Verify Eq. (2.33).
- 2.22 For the particle in a rectangular well (Section 2.4), show that in the limit $V_0 \rightarrow \infty$ (a) Eq. (2.33) gives $E = n^2 h^2 / 8ml^2$ as in Eq. (2.20); (b) the wave function goes to Eqs. (2.9) and (2.21).
- 2.23 For an electron in a 15.0-eV-deep one-dimensional rectangular well of width 2.00 Å, calculate the number of bound states. Use (6.107).
- 2.24 Find the allowed bound-state energy levels for the system of Prob. 2.23 by using a programmable calculator or computer to calculate the left side of (2.35) for ϵ going from 0 to 1 in small steps.
- 2.25 Sketch ψ for the next-lowest bound level in Fig. 2.5.
- 2.26 For a particle in a one-dimensional rectangular well, (a) must there be at least one bound state? (b) is ψ'' continuous at $x = 0$?
- 2.27 For an electron in a certain rectangular well with a depth of 20.0 eV, the lowest energy level lies 3.00 eV above the bottom of the well. Find the width of this well. *Hint:* Use $\tan \theta = \sin \theta / \cos \theta$.
- 2.28 For an electron in a certain rectangular well with a depth of 2.00 aJ, there are three bound energy levels. Find the minimum and maximum possible widths of this well. One attojoule (aJ) equals 10^{-18} J.
- 2.29 For a particle in a rectangular well of depth V_0 and width l , state whether the number of bound-state energy levels increases, decreases, or remains the same (a) as V_0 increases at fixed l ; (b) as l increases at fixed V_0 .
- 2.30 For the case $E = 0$ of a particle in a rectangular well of depth V_0 , the solution to the Schrödinger equation inside the well is $\psi_{II} = ax + b$ [see the discussion after Eq. (2.19)]. (a) Use the boundary conditions to find four equations relating the constants a and b to C and G in the equation preceding (2.32). (b) Show that if $C > 0$ (or if $C < 0$), the equations in (a) lead to the contradiction that G is both less than and greater than zero. Hence, $C = 0$. (c) Show that $C = 0$ gives $\psi = 0$ everywhere. Hence, $E = 0$ is not allowed.
- 2.31 The energy of most stars results from the fusion of hydrogen nuclei to helium nuclei. The temperature of the interior of the sun (a typical star) is 15×10^6 K. At this temperature, virtually no nuclei have enough kinetic energy to overcome the electrostatic repulsion between nuclei and approach each other closely enough to undergo fusion. Therefore, when Eddington proposed in 1920 that nuclear fusion is the source of stellar energy, his idea was rejected. Explain why fusion does occur in stars, despite the above-mentioned apparent difficulty.
- 2.32 True or false? (a) The particle-in-a-box (PIB) ground state has quantum number $n = 0$. (b) The PIB stationary-state wave functions are discontinuous at certain points. (c) The first derivative of each PIB stationary-state wave function is discontinuous at certain points. (d) The maximum probability density for every PIB stationary state is at the center of the box. (e) For the PIB $n = 2$ stationary state, the probability of finding the particle in the left quarter of the box equals the probability of finding it in the right quarter of the box. (Answer this and the next question without evaluating any integrals.) (f) For the $n = 1$ PIB stationary state, the probability of finding the particle in the left third of the box equals the probability of finding it in the middle third. (g) The wavelength of the PIB absorption transition from quantum number n to $n + 1$ decreases as the value of the quantum number n increases. (h) The probability density for the PIB stationary states is constant along the length of the box. (i) A quantum-mechanical PIB has a ground-state energy that is greater than the lowest possible energy of a classical-mechanical particle in a box.