CHAPTER 6

The Quantum Theory

> *In wave mechanics there are no impenetrable barriers, and, as the British physicist R. H. Fowler put it after my lecture on that subject at the Royal Society of London . . . "Anyone at present in this room has a finite chance of leaving it without opening the door—or, of course, without being thrown out the window."*
>
> **George Gamow**

During the early 1920s physicists strove to correct the deficiencies of Bohr's atomic model. The hydrogen atom was the subject of intensive investigation. The origination of the quantum theory, called **quantum mechanics,** is generally credited to Werner Heisenberg and Erwin Schrödinger, whose answers were clothed in very different mathematical formulations. Heisenberg (with his colleagues Max Born and Pascual Jordan) presented the *matrix formulation* of quantum mechanics in 1925. The mathematical tools necessary to introduce matrix mechanics are not intrinsically difficult, but would require too lengthy an exposition for us to study them here. The other solution, proposed in 1926 by Schrödinger, is called *wave mechanics;* its mathematical framework is similar to the classical wave descriptions we have already studied in elementary physics. Paul Dirac and Schrödinger himself (among others) later showed that the matrix and wave mechanics formulations give identical results and differ only in their mathematical form. We shall study only the formalism of Schrödinger here.

In this chapter we will determine wave functions for some simple potentials and use these wave functions to predict the values of physical observables such as position and energy. We will learn that particles are able to tunnel through potential barriers to exist in places that are not allowed by classical physics. Several applications of tunneling will be discussed.

6.1 The Schrödinger Wave Equation

After the Austrian physicist Erwin Schrödinger (Nobel Prize, 1933) learned of de Broglie's wave theory for particles, it was suggested to him while presenting a seminar in Berlin that particles must therefore obey a wave equation.

Schrödinger then quickly found a suitable wave equation based on the relationship between geometrical optics and wave optics.

In our study of elementary physics, we learned that Newton's laws, especially the second law of motion, govern the motion of particles. We need a similar set of equations to describe the wave motion of particles; that is, we need a **wave equation** that will be dependent on the potential field that the particle experiences. We can then find the wave function Ψ (discussed in the previous chapter) that will allow us to calculate the probable values of the particle's position, energy, momentum, and so on.

We must realize that although our procedure is similar to that followed in classical physics, we will no longer be able to calculate and specify the *exact* position, energy, and momentum simultaneously. Our calculations now must be consistent with the uncertainty principle and the notion of probability. We will discuss this subject again in Section 6.2, but these notions take time and experience to get used to, and we will gain that experience in this chapter.

There are several possible paths by which we could plausibly obtain the **Schrödinger wave equation.** Because none of the methods is actually a derivation, we prefer to present the equation and indicate its usefulness. Its ultimate correctness rests on its ability to explain and describe experimental results. The Schrödinger wave equation in its **time-dependent** form for a particle of energy E moving in a potential V in one dimension is

Time-dependent Schrödinger wave equation

$$i\hbar \frac{\partial \Psi(x, t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} + V\Psi(x, t) \tag{6.1}$$

where $i = \sqrt{-1}$ is an imaginary number and we have used partial derivatives. Both the potential V and wave function Ψ may be functions of space and time, $V(x, t)$ and $\Psi(x, t)$.

The extension for Equation (6.1) into three dimensions is fairly straightforward.

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2}\right) + V\Psi(x, y, z, t) \tag{6.2}$$

We will restrict ourselves to the one-dimensional form until Section 6.5.

Let's compare Equation (6.1) with the classical wave equation given by

$$\frac{\partial^2 \Psi(x, t)}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 \Psi(x, t)}{\partial t^2} \tag{6.3}$$

In this equation the wave function may be as varied as the amplitude of a water wave, a guitar-string vibration, or even the electric field **E** or magnetic field **B**. Notice that the classical wave equation contains a second-order time derivative, whereas the Schrödinger wave equation contains only a first-order time derivative. This already gives us some idea that we are dealing with a somewhat new phenomenon.

Equations (6.1) and (6.2) are the starting points that we will need for this chapter. We emphasize that the time-dependent Schrödinger wave equation (6.1) has not been derived. There is no derivation because we need *new* physical principles (such as those Newton formulated in his laws). The Schrödinger wave equation is a plausible guess that describes nature. Its worth and acceptability depend on the fact that it adequately describes experimental results. In most of the remainder of this chapter, we shall apply the Schrödinger wave equation to several simple situations in order to illustrate its usefulness.

Erwin Schrödinger (1887–1961) was an Austrian who worked at several European universities before fleeing Nazism in 1938 and accepting a position at the University of Dublin where he remained until his retirement in 1956. His primary work on the wave equation was performed during the period he was in Zurich from 1920–1927. Schrödinger worked in many fields including philosophy, biology, history, literature, and language. *AIP Emilio Segrè Visual Archives.*

Example 6.1

The wave equation must be linear for us to use the superposition principle to form wave packets using many waves. Prove that the wave equation (6.1) is linear by showing that it is satisfied for the wave function

$$\Psi(x, t) = a\Psi_1(x, t) + b\Psi_2(x, t)$$

where a and b are constants, and Ψ_1 and Ψ_2 describe two waves each satisfying Equation (6.1).

Solution: We take the derivatives needed for Equation (6.1) and insert them in a straightforward manner.

$$\frac{\partial \Psi}{\partial t} = a\frac{\partial \Psi_1}{\partial t} + b\frac{\partial \Psi_2}{\partial t}$$

$$\frac{\partial \Psi}{\partial x} = a\frac{\partial \Psi_1}{\partial x} + b\frac{\partial \Psi_2}{\partial x}$$

$$\frac{\partial^2 \Psi}{\partial x^2} = a\frac{\partial^2 \Psi_1}{\partial x^2} + b\frac{\partial^2 \Psi_2}{\partial x^2}$$

We insert these derivatives into Equation (6.1) to yield

$$i\hbar\left(a\frac{\partial \Psi_1}{\partial t} + b\frac{\partial \Psi_2}{\partial t}\right) = -\frac{\hbar^2}{2m}\left(a\frac{\partial^2 \Psi_1}{\partial x^2} + b\frac{\partial^2 \Psi_2}{\partial x^2}\right) + V(a\Psi_1 + b\Psi_2)$$

Rearrangement of this equation gives

$$a\left[i\hbar\frac{\partial \Psi_1}{\partial t} + \frac{\hbar^2}{2m}\frac{\partial^2 \Psi_1}{\partial x^2} - V\Psi_1\right] = -b\left[i\hbar\frac{\partial \Psi_2}{\partial t} + \frac{\hbar^2}{2m}\frac{\partial^2 \Psi_2}{\partial x^2} - V\Psi_2\right]$$

Because Ψ_1 and Ψ_2 each satisfy Equation (6.1), the quantities in brackets are identically zero, and Ψ is therefore also a solution. The Schrödinger wave equation cannot include any nonlinear terms in the wave functions.

In Section 5.4 we discussed wave motion and the formation of wave packets from waves. We discussed a wave of wave number k and angular frequency ω moving in the $+x$ direction.

$$\Psi(x, t) = A\sin(kx - \omega t + \phi) \tag{5.18}$$

Equation (5.18) is not the most general form of a wave function, which may include both sines and cosines. Our wave function is also not restricted to being real. Only the physically measurable quantities must be real, and Equation (6.1) already has an imaginary number. A more general form of a wave function is

$$\Psi(x, t) = Ae^{i(kx-\omega t)} = A[\cos(kx - \omega t) + i\sin(kx - \omega t)] \tag{6.4}$$

which also describes a wave moving in the $+x$ direction. In general the amplitude A may also be complex.

Example 6.2

Show that $Ae^{i(kx-\omega t)}$ satisfies the time-dependent Schrödinger wave equation.

Solution: We first take the appropriate derivatives needed for Equation (6.1).

$$\frac{\partial \Psi}{\partial t} = -i\omega Ae^{i(kx-\omega t)} = -i\omega\Psi$$

$$\frac{\partial \Psi}{\partial x} = ik\Psi$$

$$\frac{\partial^2 \Psi}{\partial x^2} = i^2k^2\Psi = -k^2\Psi$$

Inserting these results into Equation (6.1) yields

$$i\hbar(-i\omega\Psi) = -\frac{\hbar^2}{2m}(-k^2\Psi) + V\Psi$$

$$\left(\hbar\omega - \frac{\hbar^2k^2}{2m} - V\right)\Psi = 0$$

If we use $E = h\nu = \hbar\omega$ and $p = \hbar k$, we obtain

$$\left(E - \frac{p^2}{2m} - V\right)\Psi = 0$$

which is zero in our nonrelativistic formulation. Thus $e^{i(kx-\omega t)}$ appears to be an acceptable solution at this point.

We showed in Example 6.2 that $e^{i(kx-\omega t)}$ represents an acceptable solution to the Schrödinger wave equation. It is not true that all functions of $\sin(kx-\omega t)$ and $\cos(kx-\omega t)$ are solutions. We show this in the following example.

Example 6.3

Determine whether $\Psi(x, t) = A\sin(kx-\omega t)$ is an acceptable solution to the time-dependent Schrödinger wave equation.

Solution: We take the necessary derivatives needed for Equation (6.1).

$$\frac{\partial\Psi}{\partial t} = -\omega A\cos(kx-\omega t)$$

$$\frac{\partial\Psi}{\partial x} = kA\cos(kx-\omega t)$$

$$\frac{\partial^2\Psi}{\partial x^2} = -k^2A\sin(kx-\omega t) = -k^2\Psi$$

After we insert these relations into Equation (6.1), we have

$$-i\hbar\omega\cos(kx-\omega t) = \left(\frac{\hbar^2k^2}{2m} + V\right)\Psi$$

$$= \left(\frac{\hbar^2k^2}{2m} + V\right)A\sin(kx-\omega t) \qquad \textbf{(not true)} \qquad (6.5)$$

This equation is generally not satisfied for all x and t, and $A\sin(kx-\omega t)$ is, therefore, not an acceptable wave function. This function is, however, a solution to the classical wave equation (Equation [6.3]).

Normalization and Probability

We begin by reviewing the probability interpretation of the wave function that we discussed in Section 5.6. The probability $P(x)\,dx$ of a particle being between x and $x + dx$ was given in Equation (5.33).

$$P(x)\,dx = \Psi^*(x,t)\Psi(x,t)\,dx \qquad (6.6)$$

The probability of the particle being between x_1 and x_2 is given by

Probability

$$P = \int_{x_1}^{x_2} \Psi^*\Psi\,dx \qquad (6.7)$$

The wave function must also be normalized so that the probability of the particle being somewhere on the x axis is one.

Normalization

$$\int_{-\infty}^{\infty} \Psi^*(x,t)\Psi(x,t)\,dx = 1 \qquad (6.8)$$

Example 6.4

Consider a wave packet formed by using the wave function $Ae^{-\alpha|x|}$, where A is a constant to be determined by normalization. Normalize this wave function and find the probabilities of the particle being between 0 and $1/\alpha$, and between $1/\alpha$ and $2/\alpha$.

Solution: This wave function is sketched in Figure 6.1. We use Equation (6.8) to normalize Ψ.

$$\int_{-\infty}^{\infty} A^2e^{-2\alpha|x|}\,dx = 1$$

Because the wave function is symmetric about $x = 0$, we can integrate from 0 to ∞, multiply by 2, and drop the absolute value signs on $|x|$.

$$2\int_0^{\infty} A^2e^{-2\alpha x}\,dx = 1 = \frac{2A^2}{-2\alpha}\,e^{-2\alpha x}\Big|_0^{\infty}$$

$$1 = \frac{-A^2}{\alpha}(0-1) = \frac{A^2}{\alpha}$$

The coefficient $A = \sqrt{\alpha}$, and the wave function Ψ is

$$\Psi = \sqrt{\alpha}e^{-\alpha|x|}$$

We use Equation (6.7) to find the probability of the particle being between 0 and $1/\alpha$, where we again drop the absolute signs on $|x|$ because x is positive.

$$P = \int_0^{1/\alpha} \alpha e^{-2\alpha x}\, dx$$

The integration is similar to the previous one.

$$P = \frac{\alpha}{-2\alpha} e^{-2\alpha x}\Big|_0^{1/\alpha} = -\frac{1}{2}(e^{-2} - 1) = 0.432$$

The probability of the particle being between $1/\alpha$ and $2/\alpha$ is

$$P = \int_{1/\alpha}^{2/\alpha} \alpha e^{-2\alpha x}\, dx$$

$$P = \frac{\alpha}{-2\alpha} e^{-2\alpha x}\Big|_{1/\alpha}^{2/\alpha} = -\frac{1}{2}(e^{-4} - e^{-2}) = 0.059$$

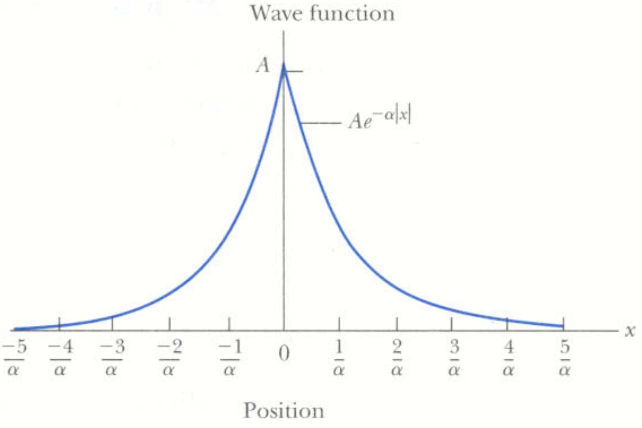


FIGURE 6.1 The wave function $Ae^{-\alpha|x|}$ is plotted as a function of x. Note that the wave function is symmetric about $x = 0$.

The wave function $e^{i(kx-\omega t)}$ represents a particle under zero net force (constant V) moving along the x axis. There is a problem with this wave function, because if we try to normalize it, we obtain an infinite result for the integral. This occurs because there is a finite probability for the particle to be anywhere along the x axis. Over the entire x axis, these finite probabilities add up, when integrated, to infinity. The only other possibility is a zero probability, but that is not an interesting physical result. Because this wave function has precise k and ω values, it represents a particle having a definite energy and momentum. According to the uncertainty principle, because $\Delta E = 0$ and $\Delta p = 0$, we must have $\Delta t = \infty$ and $\Delta x = \infty$. We cannot know where the particle is at any time. We still can use such wave functions if we restrict the particle to certain positions in space, such as in a box or in an atom. We can also form wave packets from such functions in order to localize the particle.

Properties of Valid Wave Functions

Besides the Schrödinger wave equation, there are certain properties (sometimes called **boundary conditions**) that an acceptable wave function Ψ must also satisfy. These are

1. Ψ must be finite everywhere in order to avoid infinite probabilities.
2. Ψ must be single valued in order to avoid multiple values of the probability.
3. Ψ and $\partial\Psi/\partial x$ must be continuous for finite potentials. This is required because the second-order derivative term in the wave equation must be single valued. (There are exceptions to this rule when V is infinite.)
4. In order to normalize the wave functions, Ψ must approach zero as x approaches $\pm\infty$.

Solutions for Ψ that do not satisfy these properties do not generally correspond to physically realizable circumstances.

Time-Independent Schrödinger Wave Equation

In many cases (and in most of the cases discussed here), the potential will not depend explicitly on time. The dependence on time and position can then be separated in the Schrödinger wave equation. Let

$$\Psi(x, t) = \psi(x)f(t) \tag{6.9}$$

We insert this $\Psi(x, t)$ into Equation (6.1) and obtain

$$i\hbar\psi(x)\frac{\partial f(t)}{\partial t} = -\frac{\hbar^2 f(t)}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + V(x)\psi(x)f(t)$$

We divide by $\psi(x)f(t)$ to yield

$$i\hbar\frac{1}{f(t)}\frac{df(t)}{dt} = -\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{d^2\psi(x)}{dx^2} + V(x) \tag{6.10}$$

The left side of Equation (6.10) depends only on time, the right side only on spatial coordinates. We have changed the partial derivatives to total derivatives, because each side depends only on one variable. It follows that each side must be equal to a constant (which we label B) because one variable may change independently of the other. We integrate the left side of Equation (6.10) in an effort to determine the value of B.

$$i\hbar\frac{1}{f}\frac{df}{dt} = B$$

$$i\hbar\int\frac{df}{f} = \int B\,dt$$

We integrate both sides and find

$$i\hbar\ln f = Bt$$

$$\ln f = \frac{Bt}{i\hbar}$$

From this equation we determine f to be

$$f(t) = e^{Bt/i\hbar} = e^{-iBt/\hbar} \tag{6.11}$$

If we compare this function for $f(t)$ to the free-particle wave function that has the time dependence $e^{-i\omega t}$, we see that $B = \hbar\omega = E$. This is a general result.

We now have, from Equation (6.10),

$$i\hbar\frac{1}{f(t)}\frac{df(t)}{dt} = E \tag{6.12}$$

Time-independent Schrödinger wave equation

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

Equation (6.13) is known as the **time-independent Schrödinger wave equation.**

Equation (6.11) can be rewritten as

$$f(t) = e^{-i\omega t} \tag{6.14}$$

and the wave function $\Psi(x, t)$ becomes

$$\Psi(x, t) = \psi(x)e^{-i\omega t} \tag{6.15}$$

We will restrict our attention for the present to time-independent potentials in one space dimension. Many important and useful results can be obtained from this nonrelativistic and one-dimensional form of quantum mechanics, because usually only the spatial part of the wave function $\psi(x)$ is needed. Therefore, we need only use Equation (6.13), the time-independent form of the Schrödinger wave equation.

Let's examine the probability density $\Psi^*\Psi$ discussed in Section 5.6. For the case of Equation (6.15), where the potential does not depend on time, we have

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

$$\Psi^*\Psi = \psi^2(x) \tag{6.16}$$

The probability distributions are constant in time. We have seen in introductory physics certain phenomena called *standing waves* (for example, oscillations of strings fixed at both ends). Such standing waves can be formed from traveling waves moving in opposite directions. In quantum mechanics, we say the system is in a **stationary state.**

Stationary states

Comparison of Classical and Quantum Mechanics. It is worthwhile to look briefly at the similarities and differences between classical and quantum mechanics. Newton's second law ($\mathbf{F} = d\mathbf{p}/dt$) and Schrödinger's wave equation are both differential equations. They are both postulated to explain certain observed behavior, and experiments show they are successful. Actually it is possible to derive Newton's second law from the Schrödinger wave equation, so there is no doubt which is more fundamental. Newton's laws may *seem* more fundamental—because they describe the precise values of the system's parameters, whereas the wave equation only produces wave functions which give probabilities—but by now we know from the uncertainty principle that it is not possible to simultaneously know precise values of both position and momentum and of both energy and time. Classical mechanics only appears to be more precise because it deals with macroscopic values. The underlying uncertainties in macroscopic measurements are just too small to be significant.

Ray and wave optics

An interesting parallel between classical mechanics and wave mechanics can be made by considering ray optics and wave optics. For many years in the 1700s, scientists argued which of the optics formulations was the more fundamental; Newton favored ray optics. Finally, it was shown that wave optics was the more fundamental. Ray optics is a good approximation as long as the wavelength of the radiation is much smaller than the dimensions of the apertures and obstacles it passes. Rays of light are characteristic of particlelike behavior: a narrow beam of light is formed of corpuscles. However, in order to describe interference phenomena, wave optics is required. For macroscopic objects, the de Broglie wavelength is so small that wave behavior is not apparent. However, at the atomic level, wave descriptions and quantum mechanics supplant classical mechanics. As far as we know now, there is only one correct theory: that of quantum mechanics. Classical mechanics is a good macroscopic approximation and is correct in the limit of large quantum numbers.

6.2 Expectation Values

In order to be useful, the wave equation formalism must be able to determine values of the measurable quantities like position, momentum, and energy. We shall discuss in this section how the wave function is able to provide this information. We will do this here in only one dimension, but the extension to three dimensions is straightforward. We will also evaluate the values of the physical quantities for a given time t, because in general the whole system, including the values of the physical quantities, evolves with time.

Consider a measurement of the position x of a particular system (for example, the position of a particle in a box). If we make three measurements of the position, we are likely to obtain three different results. Nevertheless, if our method of measurement is inherently *accurate*, then there is some physical significance to the *average* of our measured values of x. Moreover, the *precision* of our result improves as more measurements are made. In quantum theory we use wave functions to calculate the expected result of the average of many measurements of a given quantity. We call this result the **expectation value;** the expectation value of x is denoted by $\langle x \rangle$. Any measurable quantity for which we can calculate the expectation value is called a **physical observable.** The expectation values of physical observables (for example, position, linear momentum, angular momentum, and energy) must be real, because the experimental results of measurements are real.

Expectation value

Physical observables

Let's first review the method of determining average values. Consider a particle that is constrained to move along the x axis. If we make many measurements of the particle along the x axis, we may find the particle N_1 times at x_1, N_2 times at x_2, N_i times at x_i, and so forth. The average value of x, denoted by $\bar{x}$ [or $(x)_{\text{av}}$], is then

$$\bar{x} = \frac{N_1 x_1 + N_2 x_2 + N_3 x_3 + N_4 x_4 + \cdots}{N_1 + N_2 + N_3 + N_4 + \cdots} = \frac{\sum_i N_i x_i}{\sum_i N_i}$$

We can change from discrete to continuous variables by using the probability $P(x, t)$ of observing the particle at a particular x. The previous equation then becomes

$$\bar{x} = \frac{\int_{-\infty}^{\infty} x P(x)\,dx}{\int_{-\infty}^{\infty} P(x)\,dx} \tag{6.17}$$

In quantum mechanics we must use the probability distribution given in Equation (6.6), $P(x)\,dx = \Psi^*(x, t)\Psi(x, t)\,dx$, to determine the average or expectation value. The procedure for finding the expectation value $\langle x \rangle$ is similar to that followed in Equation (6.17):

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} x \Psi^*(x, t)\Psi(x, t)\,dx}{\int_{-\infty}^{\infty} \Psi^*(x, t)\Psi(x, t)\,dx} \tag{6.18}$$

If the wave function is normalized, the denominator becomes 1. The expectation value is then given by

$$\langle x \rangle = \int_{-\infty}^{\infty} x \Psi^*(x, t)\Psi(x, t)\,dx \tag{6.19}$$

If the wave function has not been normalized, then Equation (6.18) should be used.

The same general procedure can be used to find the expectation value of any function $g(x)$ for a normalized wave function $\Psi(x, t)$.

$$\langle g(x) \rangle = \int_{-\infty}^{\infty} \Psi^*(x, t)\, g(x)\, \Psi(x, t)\,dx \tag{6.20}$$

We emphasize again that the wave function can only provide us with the expectation value of a given function $g(x)$ that can be written as a function of x. It cannot give us the value of each individual measurement. When we say the wave function provides a complete description of the system, we mean that the expectation values of the physical observables can be determined.

Any knowledge we might have of the simultaneous values of the position x and momentum p must be consistent with the uncertainty principle. To find the expectation value of p, we first need to represent p in terms of x and t. As an example, let's consider once more the wave function of the free particle, $\Psi(x, t) = e^{i(kx-\omega t)}$. If we take the derivative of $\Psi(x, t)$ with respect to x, we have

$$\frac{\partial \Psi}{\partial x} = \frac{\partial}{\partial x}[e^{i(kx-\omega t)}] = ike^{i(kx-\omega t)} = ik\Psi$$

But because $k = p/\hbar$, this becomes

$$\frac{\partial \Psi}{\partial x} = i\frac{p}{\hbar}\Psi$$

After rearrangement, this yields

$$p[\Psi(x, t)] = -i\hbar\frac{\partial \Psi(x, t)}{\partial x}$$

An **operator** is a mathematical operation that transforms one function into another. For example, an operator, denoted by $\hat{A}$, transforms the function $f(x)$ by $\hat{A}f(x) = g(x)$. In the previous wave function equation, the quantity $-i\hbar(\partial/\partial x)$ is operating on the function $\Psi(x, t)$ and is called the *momentum operator* $\hat{p}$, where the ^ sign over the letter p indicates an operator.

$$\hat{p} = -i\hbar\frac{\partial}{\partial x} \tag{6.21}$$

Momentum operator

The existence of the momentum operator is not unique. As it happens, *each* of the physical observables has an associated operator that is used to find that observable's expectation value. In order to compute the expectation value of some physical observable A, the operator $\hat{A}$ must be placed between Ψ^* and Ψ so that it *operates* on $\Psi(x, t)$ in the order shown:

$$\langle A \rangle = \int_{-\infty}^{\infty} \Psi^*(x, t)\hat{A}\Psi(x, t)\,dx \tag{6.22}$$

Thus, the expectation value of the momentum becomes

$$\langle p \rangle = -i\hbar\int_{-\infty}^{\infty} \Psi^*(x, t)\frac{\partial \Psi(x, t)}{\partial x}\,dx \tag{6.23}$$

The position x is its own operator. Operators for observables that are functions of both x and p can be constructed from x and $\hat{p}$.

Now let's take the time derivative of the free-particle wave function.

$$\frac{\partial \Psi}{\partial t} = \frac{\partial}{\partial t}[e^{i(kx-\omega t)}] = -i\omega e^{i(kx-\omega t)} = -i\omega\Psi$$

We substitute $\omega = E/\hbar$, and then rearrange to find

$$E[\Psi(x, t)] = i\hbar\frac{\partial \Psi(x, t)}{\partial t} \tag{6.24}$$

We call the quantity operating on $\Psi(x, t)$ the *energy operator.*

Energy operator

$$\hat{E} = i\hbar \frac{\partial}{\partial t} \tag{6.25}$$

It is used to find the expectation value $\langle E \rangle$ of the energy.

$$\langle E \rangle = i\hbar \int_{-\infty}^{\infty} \Psi^*(x, t) \frac{\partial \Psi(x, t)}{\partial t}\, dx \tag{6.26}$$

Although we have found the momentum and energy operators only for the free-particle wave functions, they are general results. We shall have occasion later to use these operators.

Example 6.5

Use the momentum and energy operators with the conservation of energy to determine the Schrödinger wave equation.

Solution: We begin by setting the energy E equal to the sum of the kinetic and potential energies. Because our treatment is entirely nonrelativistic, we can write the energy as

$$E = K + V = \frac{p^2}{2m} + V \tag{6.27}$$

We allow the operators of both sides of this equation to act on the wave function. The left side gives

$$\hat{E}\,\Psi = i\hbar \frac{\partial \Psi}{\partial t} \tag{6.28}$$

The application of the operators on the right side of Equation (6.27) on Ψ gives

$$\left(\frac{1}{2m}(\hat{p})^2 + V\right)\Psi = \frac{1}{2m}\left(-i\hbar \frac{\partial}{\partial x}\right)^2 \Psi + V\Psi$$

$$= -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} + V\Psi$$

Now we set the previous equation equal to Equation (6.28) and obtain

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} + V\Psi \tag{6.29}$$

which is the time-dependent Schrödinger wave equation, Equation (6.1). It should be noted that this example is not a determination of the Schrödinger wave equation, but rather a check of the consistency of the definitions.

6.3 Infinite Square-Well Potential

We have thus far established the time-independent Schrödinger wave equation and have discussed how the wave functions can be used to determine the physical observables. Now we would like to find the wave function for several possible potentials and see what we can learn about the behavior of a system having those potentials. In the process of doing this we will find that some observables, including energy, have quantized values. We begin by exploring the simplest such system—that of a particle trapped in a box with infinitely hard walls that the particle cannot penetrate.

The potential, called an *infinite square well,* is shown in Figure 6.2 and is given by

$$V(x) = \begin{cases} \infty, & x \le 0,\ x \ge L \\ 0, & 0 < x < L \end{cases} \tag{6.30}$$

The particle is constrained to move only between $x = 0$ and $x = L$, where the particle experiences no forces. Although it is a simple potential, we will see that it is useful because so many physical situations can be approximated by it. We will learn also that requiring the wave function to satisfy certain boundary conditions leads to energy quantization. We will use this fact to explore energy levels of simple atomic and nuclear systems.

As we stated previously, most of the situations we encounter will allow us to use the time-independent Schrödinger wave equation. Such is the case here. If we insert $V = \infty$ in Equation (6.13), we see that the only possible solution for the wave function is $\psi(x) = 0$. Therefore, there is zero probability for the particle to be located at $x \leq 0$ or $x \geq L$. Because the kinetic energy of the particle must be finite, the particle can never penetrate into the region of infinite potential. However, when $V = 0$, Equation (6.13) becomes, after rearranging,

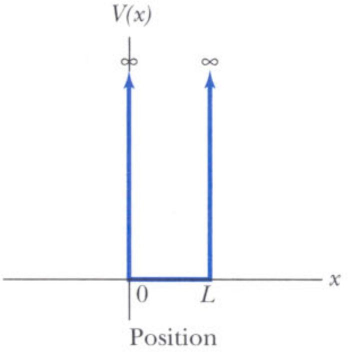


FIGURE 6.2 Infinite square well potential. Potential $V = \infty$ everywhere but $0 \leq x \leq L$, where $V = 0$.

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi = -k^2\psi$$

where we have used Equation (6.13) with $V = 0$ and let the wave number $k = \sqrt{2mE/\hbar^2}$. A suitable solution to this equation that satisfies the properties given in Section 6.1 is

$$\psi(x) = A \sin kx + B \cos kx \tag{6.31}$$

The wave function must be continuous, which means that $\psi(x) = 0$ at both $x = 0$ and $x = L$ as already discussed. The proposed solution in Equation (6.31) therefore must have $B = 0$ in order to have $\psi(x = 0) = 0$. In order for $\psi(x = L) = 0$, then $A \sin(kL) = 0$ and because $A = 0$ leads to a trivial solution, we must have

$$kL = n\pi \tag{6.32}$$

where n is a positive integer. The value $n = 0$ leads to $\psi = 0$, a physically uninteresting solution, and negative values of n do not give different physical solutions than the positive values. The wave function is now

$$\psi_n(x) = A \sin\left(\frac{n\pi x}{L}\right) \qquad n = 1,2,3, \ldots \tag{6.33}$$

The property that $d\psi/dx$ be continuous is not satisfied in this case, because of the infinite step value of the potential at $x = 0$ and $x = L$, but we were warned of this particular situation, and it creates no problem. We normalize our wave function over the total distance $-\infty < x < \infty$.

$$\int_{-\infty}^{\infty} \psi_n^*(x)\psi_n(x)\,dx = 1$$

Substitution of the wave function yields

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

This is a straightforward integral (with the help of integral tables, see Appendix 2) and gives $L/2$, so that

$$A^2 \frac{L}{2} = 1$$

and

$$A = \sqrt{\frac{2}{L}}$$

The normalized wave function becomes

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right) \qquad n = 1,2,3,\ldots \tag{6.34}$$

These wave functions are identical to the ones obtained for a vibrating string with its ends fixed that we studied in elementary physics. The application of the boundary conditions here corresponds to fitting standing waves into the box. It is not a surprise to obtain standing waves in this case, because we are considering time-independent solutions. Because $k_n = n\pi/L$ from Equation (6.32), we have

$$k_n = \frac{n\pi}{L} = \sqrt{\frac{2mE_n}{\hbar^2}}$$

Notice the subscript n on k_n and E_n denoting that they depend on the integer n and have multiple values. The previous equation is solved for E_n to yield

Quantized energy levels

$$E_n = n^2\frac{\pi^2\hbar^2}{2mL^2} \qquad n = 1,2,3,\ldots \tag{6.35}$$

The possible energies E_n of the particle, called **energy levels**, are quantized. The integer n is called a **quantum number.** Notice that the results for the quantized energy levels in Equation (6.35) are identical to those obtained in Example 5.6, when we treated a particle in a one-dimensional box as a wave. The quantization of the energy occurs in a natural way from the application of the boundary conditions (standing waves) to possible solutions of the wave equation. Each wave function $\psi_n(x)$ has associated with it a unique energy E_n. In Figure 6.3 we show the wave function ψ_n, probability density $|\psi_n|^2$, and energy E_n for the lowest three values of n (1, 2, 3).

The lowest energy level given by $n = 1$, is called the *ground state,* and its energy is given by

$$E_1 = \frac{\pi^2\hbar^2}{2mL^2}$$

Note that the lowest energy cannot be zero because we have ruled out the possibility of $n = 0$ ($\psi_0 = 0$). Classically, the particle can have zero or any positive energy. If we calculate E_n for a macroscopic object in a box (for example, a tennis ball in a tennis court), we will obtain a certain number for E_1. Adjacent energy levels would be so close together that we could not measure their differences. Actual macroscopic objects must have very large values of n.

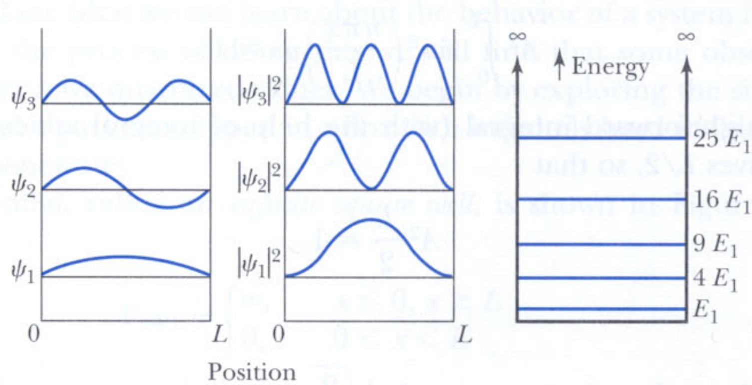


FIGURE 6.3 Wave functions ψ_n, probability densities $|\psi_n|^2$, and energy levels E_n for the lowest quantum numbers for the infinite square-well potential.

Classically, the particle has equal probability of being anywhere inside the box. The classical probability function (see Section 6.2) is $P(x) = 1/L$ (for $0 < x < L$, zero elsewhere) in order for the probability to be 1 for the particle to be in the box. According to Bohr's correspondence principle (see Section 4.4), we should obtain the same probability in the region where the classical and quantum results should agree, that is, for large n. The quantum probability is $(2/L)\sin^2(k_n x)$. For large values of n, there will be many oscillations within the box. The average value of $\sin^2\theta$ over one complete cycle is 1/2. The average value of $\sin^2\theta$ over many oscillations is also 1/2. Therefore, the quantum probability is also $1/L$ in agreement with the classical result.

Example 6.6

Show that the wave function $\Psi_n(x, t)$ for a particle in an infinite square well corresponds to a standing wave in the box.

Solution: We have just found the wave function $\psi_n(x)$ in Equation (6.34). According to Equation (6.14), we can obtain $\Psi_n(x, t)$ by multiplying the wave function $\psi_n(x)$ by $e^{-i\omega_n t}$.

$$\Psi_n(x, t) = \sqrt{\frac{2}{L}}\sin(k_n x)e^{-i\omega_n t}$$

We can write $\sin(k_n x)$ as

$$\sin(k_n x) = \frac{e^{ik_n x} - e^{-ik_n x}}{2i}$$

so that the wave function* becomes

$$\Psi_n(x, t) = \sqrt{\frac{2}{L}}\,\frac{e^{i(k_n x - \omega_n t)} - e^{-i(k_n x + \omega_n t)}}{2i}$$

This is the equation of a standing wave for a vibrating string, for example. It is the superposition of a wave traveling to the right with a wave traveling to the left. They interfere to produce a standing wave of angular frequency ω_n.

*The imaginary number i should be of little concern, because the probability values are determined by a product of $\psi^*\psi$, which gives a real number.

Example 6.7

Determine the expectation values for x, x^2, p, and p^2 of a particle in an infinite square well for the first excited state.

Solution: The first excited state corresponds to $n = 2$, because $n = 1$ corresponds to the lowest energy state or the ground state. The wave function for this case, according to Equation (6.34), is

$$\psi_2(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{2\pi x}{L}\right)$$

The expectation value $\langle x\rangle_{n=2}$ is

$$\langle x\rangle_{n=2} = \frac{2}{L}\int_0^L x\sin^2\left(\frac{2\pi x}{L}\right)dx = L/2$$

We evaluate all these integrations by looking up the integral in Appendix 3. As we expect, the average position of the particle is in the middle of the box ($x = L/2$), even though the actual probability of the particle being there is zero (see $|\psi_2|^2$ in Figure 6.3).

The expectation value $\langle x^2\rangle_{n=2}$ of the square of the position is given by

$$\langle x^2\rangle_{n=2} = \frac{2}{L}\int_0^L x^2\sin^2\left(\frac{2\pi x}{L}\right)dx = 0.32L^2$$

The value of $\sqrt{\langle x^2\rangle_{n=2}}$ is $0.57L$, larger than $\langle x\rangle_{n=2} = 0.5L$. Does this seem reasonable? (*Hint:* Look again at the shape of the wave function in Figure 6.3.)

The expectation value $\langle p\rangle_{n=2}$ is determined by using Equation (6.23).

$$\langle p\rangle_{n=2} = (-i\hbar)\frac{2}{L}\int_0^L \sin\left(\frac{2\pi x}{L}\right)\left(\frac{d}{dx}\sin\left(\frac{2\pi x}{L}\right)\right)dx$$

which reduces to

$$\langle p\rangle_{n=2} = -\frac{4i\hbar}{L^2}\int_0^L \sin\left(\frac{2\pi x}{L}\right)\cos\left(\frac{2\pi x}{L}\right)dx = 0$$

Because the particle is moving left as often as right in the box, the average momentum is zero.

The expectation value $\langle p^2 \rangle_{n=2}$ is given by

$$\langle p^2 \rangle_{n=2} = \frac{2}{L}\int_0^L \sin\left(\frac{2\pi x}{L}\right)\left(-i\hbar\frac{d}{dx}\right)\left(-i\hbar\frac{d}{dx}\right)\sin\left(\frac{2\pi x}{L}\right)dx$$

$$= (-i\hbar)^2\frac{2}{L}\int_0^L \sin\left(\frac{2\pi x}{L}\right)\left(\frac{2\pi}{L}\frac{d}{dx}\right)\cos\left(\frac{2\pi x}{L}\right)dx$$

$$= -(-\hbar^2)\,\frac{8\pi^2}{L^3}\int_0^L \sin\left(\frac{2\pi x}{L}\right)\sin\left(\frac{2\pi x}{L}\right)dx$$

$$= \frac{4\pi^2\hbar^2}{L^2}$$

This value can be compared with E_2 (Equation (6.35)),

$$E_2 = \frac{4\pi^2\hbar^2}{2mL^2} = \frac{\langle p^2 \rangle_{n=2}}{2m}$$

which is correct, because nonrelativistically we have $E = p^2/2m + V$ and $V = 0$.

Example 6.8

A typical diameter of a nucleus is about 10^{-14} m. Use the infinite square well potential to calculate the transition energy from the first excited state to the ground state for a proton confined to the nucleus.

Solution: The energy of the ground state, from Equation (6.35), is

$$E_1 = \frac{\pi^2\hbar^2c^2}{2mc^2L^2} = \frac{1}{mc^2}\,\frac{\pi^2(197.3\ \text{eV}\cdot\text{nm})^2}{2(10^{-5}\ \text{nm})^2}$$

$$= \frac{1}{mc^2}(1.92\times10^{15}\ \text{eV}^2)$$

The mass of the proton is 938.3 MeV/c^2 which gives

$$E_1 = \frac{1.92\times10^{15}\ \text{eV}^2}{938.3\times10^6\ \text{eV}} = 2.0\ \text{MeV}$$

The first excited state energy is found from $E_2 = 4E_1 = 8$ MeV, and the transition energy is $\Delta E = E_2 - E_1 = 6$ MeV. This value is a reasonable one for protons in the nucleus. If we had done a similar calculation for an electron in the nucleus, we would find energies on the order of 10^4 MeV, much larger than the rest energy of the electron. A correct relativistic treatment is necessary, and it would give electron energies of significantly less than 10^4 MeV but still much larger than those electrons actually observed being emitted from the nucleus in β decay. Such reasoning indicates that electrons do not exist inside the nucleus.

6.4 Finite Square-Well Potential

We gained some experience in the last section in dealing with the time-independent Schrödinger wave equation. Now we want to look at a more realistic potential—one that is not infinite. The finite square-well potential is similar to the infinite one, but we let the potential be V_0 rather than infinite in the region $x \leq 0$ and $x \geq L$.

$$V(x) = \begin{cases} V_0 & x \leq 0 \qquad \text{region I} \\ 0 & 0 < x < L \qquad \text{region II} \\ V_0 & x \geq L \qquad \text{region III} \end{cases} \tag{6.36}$$

The three regions of the potential are shown in Figure 6.4. We will consider a particle of energy $E < V_0$ that classically is bound inside the well. We will find that quantum mechanics *allows the particle to be outside the well.* We set the potential $V = V_0$ in the time-independent Schrödinger Equation (6.13) for regions I and III outside the square well. This gives

$$-\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{d^2\psi}{dx^2} = E - V_0 \qquad \text{regions I, III} \tag{6.37}$$

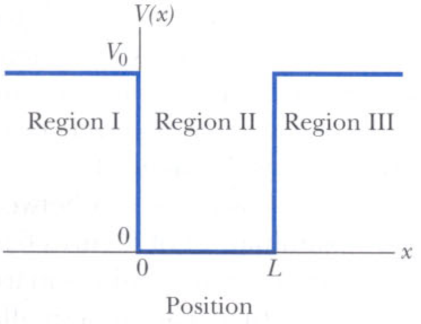


FIGURE 6.4 A finite square-well potential has the value V_0 everywhere except $0 < x < L$, where $V = 0$. The three regions I, II, and III are indicated.

We rewrite this using $\alpha^2 = 2m(V_0 - E)/\hbar^2$, a positive constant.

$$\frac{d^2\psi}{dx^2} = \alpha^2\psi$$

The solution to this differential equation has exponentials of the form $e^{\alpha x}$ and $e^{-\alpha x}$. In the region $x > L$, we can reject the positive exponential term, because it would become infinite as $x \longrightarrow \infty$. Similarly, the negative exponential can be rejected for $x < 0$. The wave functions become

$$\psi_{\text{I}}(x) = Ae^{\alpha x} \qquad \text{region I, } x < 0 \tag{6.38}$$

$$\psi_{\text{III}}(x) = Be^{-\alpha x} \qquad \text{region III, } x > L \tag{6.39}$$

Inside the square well, where the potential V is zero, the wave equation becomes

$$\frac{d^2\psi}{dx^2} = -k^2\psi$$

where $k = \sqrt{(2mE)/\hbar^2}$. Instead of a sinusoidal solution, we can write it as

$$\psi_{\text{II}} = Ce^{ikx} + De^{-ikx} \qquad \text{region II, } 0 < x < L \tag{6.40}$$

We now want to satisfy the properties of Section 6.1. We have already made sure that all but properties 2 and 3 have been satisfied. The wave functions are finite throughout the x region, even at infinity. In order for the wave functions to be single valued, we must have $\psi_{\text{I}} = \psi_{\text{II}}$ at $x = 0$ and $\psi_{\text{II}} = \psi_{\text{III}}$ at $x = L$. Both ψ and $\partial\psi/\partial x$ must be continuous at $x = 0$ and $x = L$. We will not perform these tedious procedures here, but the results for the wave functions are presented graphically in Figure 6.5.

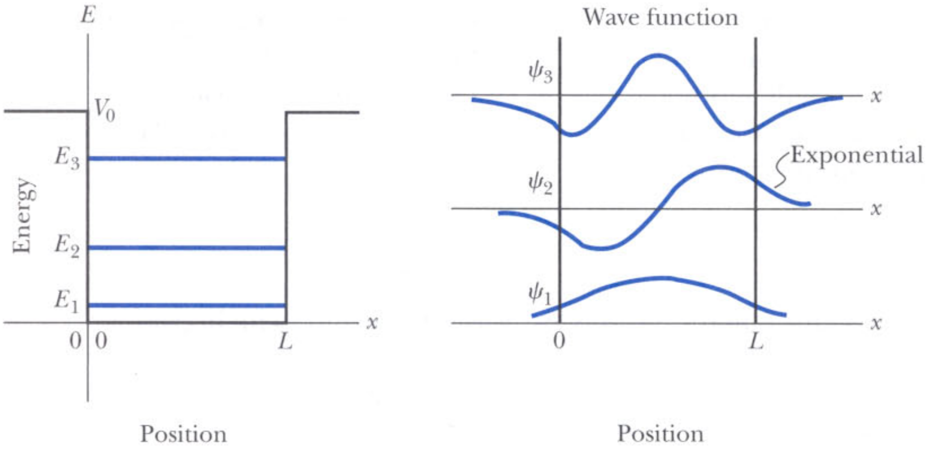


FIGURE 6.5 The energy levels E_n and wave functions ψ_n for the lowest quantum numbers for the finite square-well potential. Notice that ψ extends past $x < 0$ and $x > L$, where classically the particle is forbidden. *From R. Eisberg and R. Resnick, Quantum Physics of Atoms, Molecules, Solids, Nuclei, and Particles, 2nd ed. New York: Wiley, 1985.*

The application of the boundary conditions leads to quantized energy values E_n and to particular wave functions $\psi_n(x)$. One remarkable result is that the particle has a finite probability of being outside the square well, as is indicated by Figure 6.5. Notice that the wave functions join smoothly at the edges of the well and decrease exponentially outside the well.

What other differences can we easily discern between the infinite and finite square well? For example, by examination of Figures 6.5 and 6.3, we can see that the de Broglie wavelength is larger for the finite square well because the waves extend past the square well. This in turn leads to a smaller momentum and lower energy levels. The number of energy levels will, of course, be limited because of the potential height V_0 (see Figure 6.5). When $E > V_0$ the particle is unbound, a situation that will be discussed in Section 6.7.

The occurrence of the particle outside the square well is clearly prohibited classically, but it occurs naturally in quantum mechanics. Note that because of the exponential decrease of the wave functions ψ_{I} and ψ_{III}, the probability of the particle penetrating a distance greater than $\delta x \approx 1/\alpha$ begins to decrease markedly.

$$\delta x \approx \frac{1}{\alpha} = \frac{\hbar}{\sqrt{2m(V_0 - E)}} \tag{6.41}$$

However, we will later find values of δx as large as $10/\alpha$ and $20/\alpha$ for electrons tunneling through semiconductors (Example 6.11) and for nuclear alpha decay (Example 6.13), respectively. The fraction of particles that successfully tunnel through in these cases is exceedingly small, but the results are quite important.

It should not be surprising to find that the penetration distance that violates classical physics is proportional to Planck's constant $\hbar$. This result is also consistent with the uncertainty principle, because, in order for the particle to be in the barrier region, the uncertainty ΔE of the energy must be very large. According to the uncertainty principle ($\Delta E\, \Delta t \geq \hbar/2$), this can only occur for a very short period of time Δt.

6.5 Three-Dimensional Infinite-Potential Well

In order to use quantum theory to solve the atomic physics problems that we shall face in Chapters 7 and 8, it is necessary to extend the Schrödinger equation to three dimensions. This is easily accomplished with the operator notation already developed in Section 6.2. After obtaining the three-dimensional equation, we shall use it to study the problem of a three-dimensional infinite-potential well.

We anticipate that there will be time-independent solutions, so we shall start with the time-independent Schrödinger wave equation. The wave function ψ must be a function of all three spatial coordinates, that is, $\psi = \psi(x, y, z)$. We could just directly modify Equation (6.13) to three dimensions, but we prefer to use a simple method to arrive at the Schrödinger equation. We begin with the conservation of energy.

$$E = K + V = \frac{p^2}{2m} + V$$

We multiply this equation times the wave function ψ which gives

$$\frac{p^2}{2m}\psi + V\psi = E\psi \tag{6.42}$$

We now use Equation (6.22) to express p^2 as an operator to act on ψ. But because $p^2 = p_x^{\,2} + p_y^{\,2} + p_z^{\,2}$, we must apply the momentum operator in all three dimensions.

$$\hat{p}_x\psi = -i\hbar\,\frac{\partial\psi}{\partial x}$$

$$\hat{p}_y\psi = -i\hbar\,\frac{\partial\psi}{\partial y}$$

$$\hat{p}_z\psi = -i\hbar\,\frac{\partial\psi}{\partial z}$$

The application of $\hat{p}^2$ in Equation (6.42) gives

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) + V\psi = E\psi \tag{6.43}$$

Time-independent Schrödinger wave equation in three dimensions

This is the time-independent Schrödinger wave equation in three dimensions.

You may recognize the expression in parentheses as the Laplacian operator in mathematics. It is usually written with the shorthand notation

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{6.44}$$

With this notation, we can write

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi \tag{6.45}$$

Example 6.9

Consider a free particle inside a box with lengths L_1, L_2, and L_3 along the x, y, and z axes, respectively, as shown in Figure 6.6. The particle is constrained to be inside the box. Find the wave functions and energies. Then find the ground energy and wave function and the first excited state energy for a cube of sides L.

Solution: Inside the box $V = 0$, so the wave equation we must solve is

$$-\frac{\hbar^2}{2m}\nabla^2\psi = E\psi \tag{6.46}$$

We employ some of the same strategies to solve this problem as we used for the one-dimensional case. First, because we are considering the walls of the box to be absolutely closed, they are infinite potential barriers, and the wave function ψ must be zero at the walls and outside. We expect to see standing waves similar to Equation (6.31).

But how should we write the wave function so as to properly include the x, y, and z dependence of the wave function? In this case the mathematics will follow from the physics. The particle is free within the box. Therefore, the x-, y-, and z-dependent parts of the wave function must be independent of each other. It is therefore reasonable to try a wave function of the form

$$\psi(x, y, z) = A\sin(k_1x)\sin(k_2y)\sin(k_3z) \tag{6.47}$$

where A is a normalization constant. The quantities $k_i\,(i = 1, 2, 3)$ are determined by applying the appropriate boundary conditions. For example, the condition that $\psi = 0$ at $x = L_1$ requires that $k_1L_1 = n_1\pi$ or $k_1 = n_1\pi/L_1$. The values for the k_i are

$$k_1 = \frac{n_1\pi}{L_1} \qquad k_2 = \frac{n_2\pi}{L_2} \qquad k_3 = \frac{n_3\pi}{L_3} \tag{6.48}$$

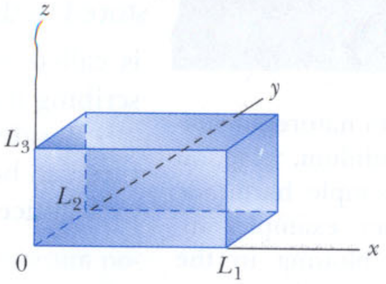


FIGURE 6.6 A three-dimensional box that contains a free particle. The potential is infinite outside the box, so the particle is constrained to be inside the box.

where n_1, n_2, and n_3 are integers. Not surprisingly, we have found that in three dimensions, it is necessary to use *three* quantum numbers to describe the physical state.

To find the energies, we simply substitute the wave function into the Schrödinger equation and solve for E. If we do this in Equation (6.43), we find

$$E = \frac{\pi^2\hbar^2}{2m}\left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} + \frac{n_3^2}{L_3^2}\right) \qquad (6.49)$$

The allowed energy values also depend on the values of the three quantum numbers n_1, n_2, and n_3.

Let us now consider the special case of the *cubical* box, with $L_1 = L_2 = L_3 \equiv L$. The energy values of Equation (6.49) can be expressed

$$E = \frac{\pi^2\hbar^2}{2mL^2}\left(n_1^2 + n_2^2 + n_3^2\right) \qquad (6.50)$$

For the ground state we have $n_1 = n_2 = n_3 = 1$, so the ground state energy is

$$E_{\text{gs}} = \frac{3\pi^2\hbar^2}{2mL^2} \qquad (6.51)$$

and the ground state wave function is

$$\psi_{\text{gs}} = A\sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{\pi y}{L}\right)\sin\left(\frac{\pi z}{L}\right) \qquad (6.52)$$

What is the energy of the first excited state? Higher values of the quantum numbers n_i correspond to higher energies, therefore, it is logical to try something like $n_1 = 2$, $n_2 = 1$, and $n_3 = 1$. But we could just as well assign quantum numbers $n_1 = 1$, $n_2 = 2$, $n_3 = 1$ to the first excited state, or $n_1 = 1$, $n_2 = 1$, $n_3 = 2$. In each of these cases the total energy is

$$E_{\text{1st}} = \frac{\pi^2\hbar^2}{2mL^2}\left(2^2 + 1^2 + 1^2\right) = \frac{3\pi^2\hbar^2}{mL^2}$$

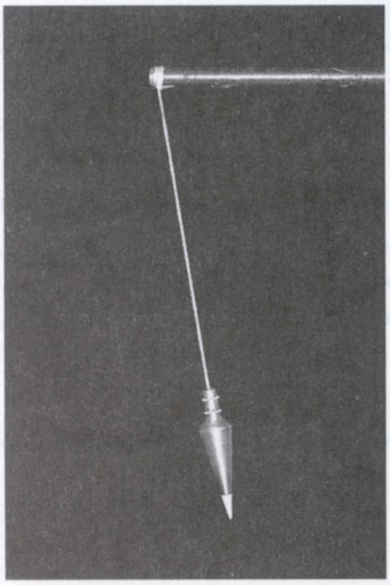
Degenerate state

In physics we say that a given state is **degenerate** when there is more than one wave function for a given energy. We have this situation in the previous example, where all three possible wave functions for the first excited state have the same energy. The degeneracy in this case is a result of the symmetry of the cube. If the box had sides of three different lengths, we say the *degeneracy* is removed, because the three quantum numbers in different orders would result in three different energies. Degeneracy is not a new phenomenon. It also occurs in classical physics, for example, in planetary motion. Degeneracy results from particular properties of the potential energy function that describes the system. A *perturbation* of the potential energy can remove the degeneracy. Energy levels can be split (and the degeneracy removed) by applying external magnetic fields (Zeeman effect, Section 7.4) and external electric fields (Stark effect, Special Topic on Rydberg Atoms, Chapter 7).

6.6 Simple Harmonic Oscillator

Because of their wide occurrence in nature, we now want to examine simple harmonic oscillators. We have already studied in introductory physics the case of a mass oscillating in one dimension on the end of a spring. Consider a spring having spring constant κ* that is in equilibrium at $x = x_0$. The restoring force (see Figure 6.7a) along the x direction is $F = -\kappa(x - x_0)$, and the potential energy stored in the spring is $V = \kappa(x - x_0)^2/2$ (see Figure 6.7b). The resulting motion is called *simple harmonic motion* (abbreviated as SHM), and the equations describing it are well known.

Besides springs and pendula (small oscillations), many phenomena in nature can be approximated by SHM, for example, diatomic molecules and atoms in a lattice. Systems can also be approximated by SHM in a general way. As an



Many things in nature, including this pendulum, respond naturally in simple harmonic motion. Other examples include leaves blowing in the wind and atoms vibrating in molecules. *Leonard Lessin/Peter Arnold, Inc.*

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*We let κ be the spring constant in this section rather than the normal k to avoid confusion with the wave number. It is important to note the context in which variables like k and κ are used, because either might be used as wave number or spring constant.

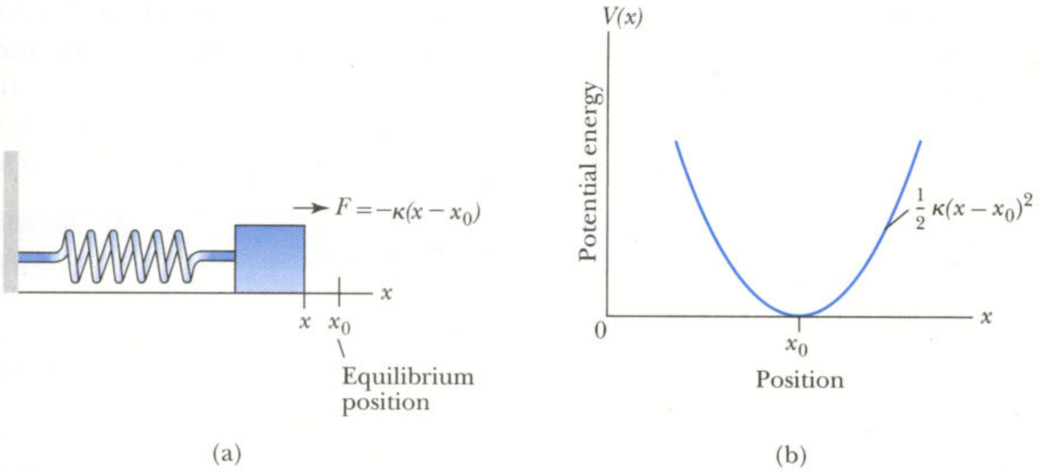


FIGURE 6.7 (a) The restoring force for a spring having a spring constant κ is $F = -\kappa(x - x_0)$. (b) The potential energy has the form $\kappa(x - x_0)^2/2$.

example, consider a lattice in which the force on the atoms depends on the distance x from some equilibrium position x_0. If we expand the potential in a Taylor series in terms of the distance $(x - x_0)$ from equilibrium, we obtain

$$V(x) = V_0 + V_1(x - x_0) + \frac{1}{2} V_2(x - x_0)^2 + \cdots \tag{6.53}$$

where V_0, V_1, and V_2 are constants, and we have kept only the three lowest terms of the series, because $(x - x_0) \approx 0$ for small excursions from the equilibrium position x_0. At $x = x_0$ we have equilibrium (e.g., a minimum of the potential), so $(dV/dx) = 0$ at $x = x_0$. This requires that $V_1 = 0$, and if we redefine the zero of potential energy to require $V_0 = 0$, then the lowest term of the potential $V(x)$ is

$$V(x) = \frac{1}{2}V_2(x - x_0)^2$$

This is the origin of the $V = \kappa x^2/2$ potential energy term that occurs so often. Near the equilibrium position many potentials may be approximated by a parabolic form as displayed in Figure 6.8.

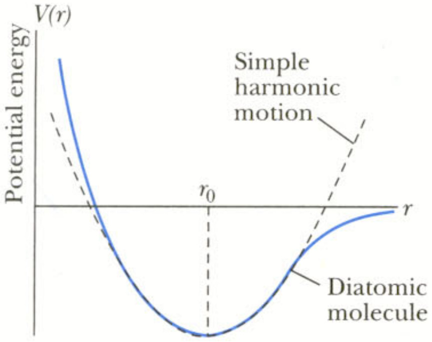


FIGURE 6.8 Many potentials in nature can be approximated near their equilibrium position by the simple harmonic potential (black dashed curve). Such is the case here for the potential energy $V(r)$ of a diatomic molecule near its equilibrium position r_0 (blue curve).

We want to study the quantum description of simple harmonic motion by inserting a potential $\kappa x^2/2$ (we let $x_0 = 0$, see Figure 6.9a) into the time-independent Schrödinger wave equation (6.13).

$$\frac{d^2\psi}{dx^2} = -\frac{2m}{\hbar^2}\left(E - \frac{\kappa x^2}{2}\right)\psi = \left(-\frac{2mE}{\hbar^2} + \frac{m\kappa x^2}{\hbar^2}\right)\psi \tag{6.54}$$

If we let

$$\alpha^2 = \frac{m\kappa}{\hbar^2} \tag{6.55a}$$

and

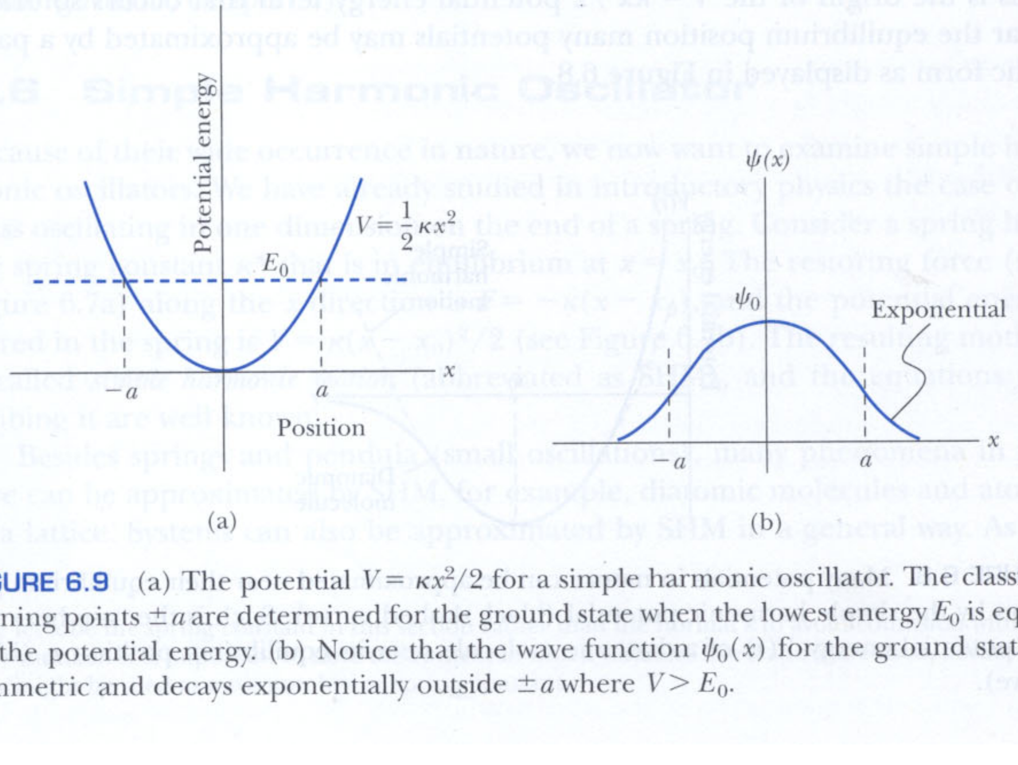
$$\beta = \frac{2mE}{\hbar^2} \tag{6.55b}$$

then

$$\frac{d^2\psi}{dx^2} = (\alpha^2 x^2 - \beta)\psi \tag{6.56}$$

Before discussing the solution of Equation (6.56), let us first examine what we can learn about the problem qualitatively. Because the particle is confined to the potential well, centered at $x = 0$, it has zero probability of being at $x = \infty$. Therefore, $\psi(x) \to 0$ as $x \to \infty$.

What is the lowest energy level possible for the harmonic oscillator? Is $E = 0$ possible? If $E = 0$, then $x = 0$ and $V = 0$ in order to allow $E \geq V$. But if E and V are zero, then K.E. $= 0$, and the momentum $p = 0$. Having both $x = 0$ and $p = 0$ (that is, both x and p are known exactly) simultaneously violates the uncertainty principle. Therefore, the minimum energy E cannot be zero. In fact, the energy levels must all be positive, because $E > V \geq 0$. The state having the lowest energy, denoted here by E_0, will have an energy like that shown in Figure 6.9a, and the wave function ψ_0 for that state will most likely be a simple wave fitting inside the region defined by the potential (see Figure 6.9b). Let $E_0 = V_0 = \kappa a^2/2$. The distances $\pm a$ define the classical limits of the particle, but we know from the previous section that the particle has a small probability of being outside the potential well dimensions of $\pm a$. Therefore, the wave function will not be zero at



(a) (b)

FIGURE 6.9 (a) The potential $V = \kappa x^2/2$ for a simple harmonic oscillator. The classical turning points $\pm a$ are determined for the ground state when the lowest energy E_0 is equal to the potential energy. (b) Notice that the wave function $\psi_0(x)$ for the ground state is symmetric and decays exponentially outside $\pm a$ where $V > E_0$.

$x = \pm a$, but will have a finite value that decreases rapidly to zero on the other side of the barrier. Thus a plausible guess for the lowest-order wave function ψ_0 is like that shown in Figure 6.9b. We find the minimum energy E_0, called the *zero-point energy,* in the next example.

Example 6.10

Estimate the minimum energy of the simple harmonic oscillator allowed by the uncertainty principle.

Solution: In introductory physics we learned that the average kinetic energy is equal to the average potential energy for simple harmonic oscillators over the range of motion (from $-x$ to $+x$), and both the average potential and kinetic energies are equal to one half the total energy.

$$\frac{1}{2}E = \frac{1}{2}\kappa(x^2)_{\text{av}} = \frac{1}{2m}(p^2)_{\text{av}}$$

The mean value of x is zero, but the mean value of $(x^2)_{\text{av}}$ is the mean square deviation $(\Delta x)^2$. Similarly, $(p^2)_{\text{av}} = (\Delta p)^2$. From the previous equation, we therefore have the energy $E = \kappa(\Delta x)^2 = (\Delta p)^2/m$ and, as a result, we must have $\Delta x = \Delta p/\sqrt{m\kappa}$. From the uncertainty principle $\Delta p \Delta x \geq \hbar/2$, and the minimum value of $\Delta x = \hbar/2\Delta p$. Now we have for the lowest energy E_0,

$$E_0 = \kappa(\Delta x)^2 = \kappa\left(\frac{\Delta p}{\sqrt{mk}}\right)\left(\frac{\hbar}{2\Delta p}\right)$$

$$E_0 = \frac{\hbar}{2}\sqrt{\frac{\kappa}{m}} = \frac{\hbar\omega}{2}$$

Our estimate for the zero-point energy of the harmonic oscillator is $\hbar\omega/2$. This agrees with the zero-point energy found by more rigorous means.

The zero-point energy is not just a curious oddity. For example, the zero-point energy for ^{4}He is large enough to prevent liquid ^{4}He from freezing at atmospheric pressure, no matter how cold the system, even near 0 K.

The wave function solutions ψ_n for Equation (6.56) are

$$\psi_n = H_n(x)e^{-\alpha x^2/2} \tag{6.57}$$

where $H_n(x)$ are polynomials of order n, where n is an integer ≥ 0. The functions $H_n(x)$ are related by a constant to the *Hermite polynomial functions* tabulated in many quantum mechanics books. The first few values of ψ_n and $|\psi_n|^2$ are shown in Figure 6.10. In contrast to the particle in a box, where the oscillatory wave function is a sinusoidal curve, in this case the oscillatory behavior is due to the polynomial, which dominates at small x, and the exponential tail is provided by the Gaussian function, which dominates at large x.

The energy levels are given by

$$E_n = \left(n + \frac{1}{2}\right)\hbar\sqrt{\kappa/m} = \left(n + \frac{1}{2}\right)\hbar\omega \tag{6.58}$$

where $\omega^2 = \kappa/m$, and ω is the classical angular frequency. From Equation (6.58) we see that the *zero-point energy* E_0 is

$$E_0 = \frac{1}{2}\hbar\omega \tag{6.59}$$

Notice that this result for E_0 is precisely the value found in Example 6.10 by using the uncertainty principle. The uncertainty principle is solely responsible for the minimum energy of the simple harmonic oscillator. In Section 5.7 we mentioned that the minimum value (that is, the equality sign) of the uncertainty principle is found for Gaussian wave packets. We note here that the wave

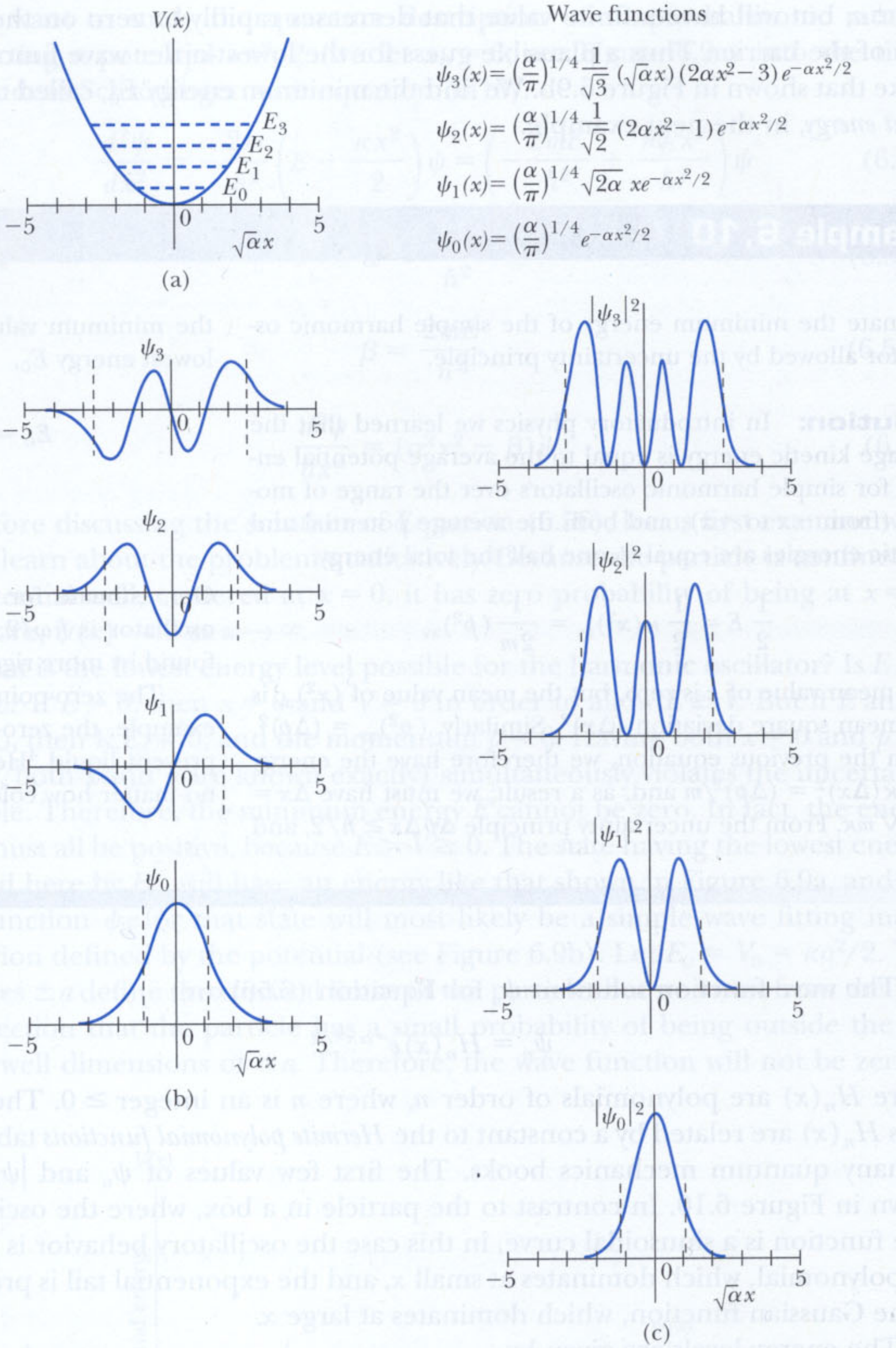


FIGURE 6.10 Results for simple harmonic oscillator potential. (a) The energy levels for the lowest four energy states are shown with the corresponding wave functions listed. (b) The wave functions for the four lowest energy states are displayed. Notice that even quantum numbers have symmetric $\psi_n(x)$, and the odd quantum numbers have antisymmetric $\psi_n(x)$. (c) The probability densities $|\psi_n|^2$ for the lowest four energy states are displayed.

functions for the simple harmonic oscillators are of just the Gaussian form (see Figure 6.10). The minimum energy E_0 allowed by the uncertainty principle, sometimes called the *Heisenberg limit,* is found for the ground state of the simple harmonic oscillator.

Finally, let us compare the motion as described by classical and quantum theory. Classically, we recall the motion of the mass at the end of a spring. The speed is greatest as it passes through its equilibrium position. The speed is lowest (zero) at the two ends (compressed or extended positions of the spring), as the mass stops and reverses direction. Classically, the probability of finding the mass is greatest at the ends of motion and smallest at the center (that is, proportional to the amount of time the mass spends at each position). The classical probability is shown by the black dashed line in Figure 6.11.

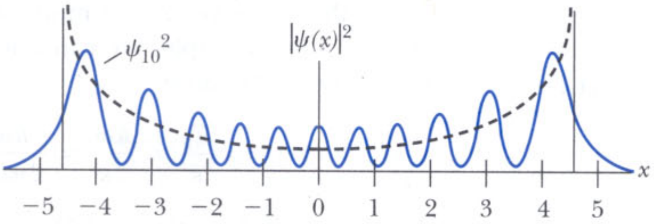


FIGURE 6.11 The probability distribution $|\psi_{10}|^2$ for the $n = 10$ state is compared with the classical probability (dashed line). As n increases, the two probability distributions become more similar.

The quantum theory probability density for the lowest energy state ($\psi_0{}^2$, see Figure 6.10) is completely contrary to the classical one. The largest probability is for the particle to be at the center. We are not surprised to see such a marked difference between classical (see Section 4.4) and quantum predictions. However, from the correspondence principle we would expect the classical and quantum probabilities to be similar as the quantum number n becomes very large. In Figure 6.11 we show $\psi_n{}^2$ for the case of $n = 10$, and we see that the average probabilities become similar. As n continues to increase, the peaks and valleys of the quantum probabilities are hardly observable, and the average value mirrors the classical result.

Example 6.11

Normalize the ground state wave function ψ_0 for the simple harmonic oscillator and find the expectation values $\langle x\rangle$ and $\langle x^2\rangle$.

Solution: Let's assume that all we know about the wave function ψ_0 is the form given in Equation (6.57). $H_0(x)$ has no dependence on x, so we take it to be a constant A. The ground state wave function is then

$$\psi_0(x) = Ae^{-\alpha x^2/2}$$

We must normalize in order to determine A.

$$\int_{-\infty}^{\infty} \psi_0^*(x)\,\psi_0(x)\,dx = 1$$

$$A^2 \int_{-\infty}^{\infty} e^{-\alpha x^2} dx = 1$$

$$2A^2 \int_{0}^{\infty} e^{-\alpha x^2} dx = 1$$

We determine this integral with the help of integral tables (see Appendix 6), with the result:

$$2A^2\left(\frac{1}{2}\sqrt{\frac{\pi}{\alpha}}\right) = 1$$

$$A^2 = \sqrt{\frac{\alpha}{\pi}}$$

$$A = \left(\frac{\alpha}{\pi}\right)^{1/4}$$

This gives for the ground state wave function,

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} \qquad (6.60)$$

This is precisely the wave function given in Figure 6.10 and is of the Gaussian form.

The expectation value of x is

$$\langle x\rangle = \int_{-\infty}^{\infty} \psi_0^*(x)\,x\,\psi_0(x)\,dx$$

$$= \sqrt{\frac{\alpha}{\pi}} \int_{-\infty}^{\infty} xe^{-\alpha x^2} dx$$

The value of $\langle x\rangle$ must be zero, because we are integrating an odd function of x over symmetric limits from $-\infty$ to $+\infty$ (see Appendix 6). Both classical and quantum mechanics predict the average value of x to be zero because of the symmetric nature of the potential, $\kappa x^2/2$.

The expectation value $\langle x^2\rangle$, however, should be positive.

$$\langle x^2\rangle = \int_{-\infty}^{\infty} \psi_0^*(x)\,x^2\psi_0(x)\,dx = \sqrt{\frac{\alpha}{\pi}} \int_{-\infty}^{\infty} x^2e^{-\alpha x^2} dx$$

$$= 2\sqrt{\frac{\alpha}{\pi}} \int_{0}^{\infty} x^2e^{-\alpha x^2} dx$$

This integral can be found in a table of integrals (see Appendix 6), and the result is

$$\langle x^2\rangle = 2\sqrt{\frac{\alpha}{\pi}}\left(\frac{\sqrt{\pi}}{4\alpha^{3/2}}\right) = \frac{1}{2\alpha}$$

Inserting the value of the constant α from Equation (6.55a) gives

$$\langle x^2\rangle = \frac{\hbar}{2\sqrt{m\kappa}}$$

Because $\omega = \sqrt{\kappa/m}$, we have

$$\langle x^2 \rangle = \frac{\hbar}{2m\omega} \tag{6.61}$$

In Example 6.10 we argued that

$$(x^2)_{\text{av}} = (\Delta x)^2 = \frac{E_0}{\kappa}$$

and showed that $E_0 = \hbar\omega/2$, the minimum energy allowed by the uncertainty principle. We can now see that these results are consistent, because

$$\langle x^2 \rangle = (x^2)_{\text{av}} = \frac{E_0}{\kappa} = \frac{\hbar\omega}{2\kappa} = \frac{\hbar\omega}{2m\omega^2} = \frac{\hbar}{2m\omega}$$

as we determined in Equation (6.61).

6.7 Barriers and Tunneling

Potential Barrier with $E > V_0$

Consider a particle of energy E approaching a potential barrier of height V_0 for $0 < x < L$. The potential elsewhere is zero. First, let us consider the case where the particle's energy is $E > V_0$ as shown in Figure 6.12. Classically we know the particle would pass the barrier, moving with reduced velocity in the region of $V_0(mv^2/2 = E - V_0$, rather than $mv^2/2 = E)$. On the other side of the barrier, where $V = 0$, the particle will have its original velocity again. According to quantum mechanics, the particle will behave differently because of its wavelike character. In regions I and III (where $V = 0$) the wave numbers are

$$k_{\text{I}} = k_{\text{III}} = \frac{\sqrt{2mE}}{\hbar} \qquad \text{where } V = 0 \tag{6.62a}$$

In the barrier region, however, we have

$$k_{\text{II}} = \frac{\sqrt{2m(E - V_0)}}{\hbar} \qquad \text{where } V = V_0 \tag{6.62b}$$

We can consider an analogy with optics. When light in air penetrates another medium (for example, glass), the wavelength changes because of the index of refraction. Some of the light will be reflected, and some will be transmitted into the medium. Because we must consider the wave behavior of particles interacting with potential barriers, we might expect similar behavior. The wave function will consist of an incident wave, a reflected wave, and a transmitted wave (see Figure 6.13). These wave functions can be determined by solving the Schrödinger wave equation, subject to appropriate boundary conditions. The difference from classical wave theories is that the wave function allows us to compute only probabilities.

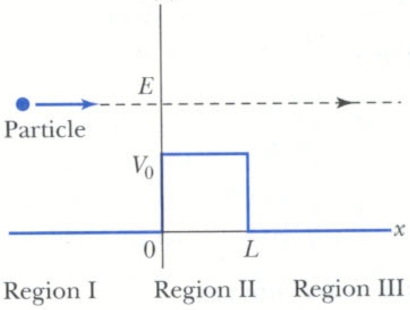


FIGURE 6.12 A particle having energy E approaches a potential barrier of width L and height V_0 with $E > V_0$. The one-dimensional space is divided into three regions as shown.

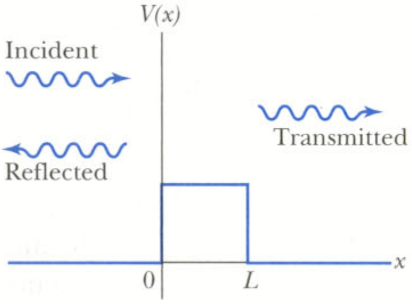


FIGURE 6.13 The incident particle in Figure 6.12 can be either transmitted or reflected.

Classical mechanics allows *no* reflection if $E > V_0$ and *total* reflection for $E < V_0$. Quantum mechanics predicts *almost total* transmission for $E \gg V_0$ and *almost complete* reflection for $E \ll V_0$. In the regime where E is comparable to V_0, unusual nonclassical phenomena may appear.

The potentials and the Schrödinger equation for the three regions are as follows:

$$\text{Region I } (x < 0) \qquad V = 0 \qquad \frac{d^2\psi_{\text{I}}}{dx^2} + \frac{2m}{\hbar^2}E\psi_{\text{I}} = 0$$

$$\text{Region II } (0 < x < L) \qquad V = V_0 \qquad \frac{d^2\psi_{\text{II}}}{dx^2} + \frac{2m}{\hbar^2}(E - V_0)\psi_{\text{II}} = 0$$

$$\text{Region III } (x > L) \qquad V = 0 \qquad \frac{d^2\psi_{\text{III}}}{dx^2} + \frac{2m}{\hbar^2}E\psi_{\text{III}} = 0$$

The wave functions obtained for these equations are

$$\text{Region I } (x < 0) \qquad \psi_{\text{I}} = Ae^{ik_{\text{I}}x} + Be^{-ik_{\text{I}}x} \tag{6.63a}$$

$$\text{Region II } (0 < x < L) \qquad \psi_{\text{II}} = Ce^{ik_{\text{II}}x} + De^{-ik_{\text{II}}x} \tag{6.63b}$$

$$\text{Region III } (x > L) \qquad \psi_{\text{III}} = Fe^{ik_{\text{I}}x} + Ge^{-ik_{\text{I}}x} \tag{6.63c}$$

We assume that we have incident particles coming from the left moving along the $+x$ direction. In this case the term $Ae^{ik_{\text{I}}x}$ in region I represents the incident particles. The term $Be^{-ik_{\text{I}}x}$ represents the reflected particles moving in the $-x$ direction. In region III there are no particles initially moving along the $-x$ direction, so the only particles present must be those transmitted through the barrier. Thus $G = 0$, and the only term in region III is $Fe^{ik_{\text{I}}x}$. We summarize these wave functions:

$$\text{Incident wave} \qquad \psi_{\text{I}}(\text{incident}) = Ae^{ik_{\text{I}}x} \tag{6.64a}$$

$$\text{Reflected wave} \qquad \psi_{\text{I}}(\text{reflected}) = Be^{-ik_{\text{I}}x} \tag{6.64b}$$

$$\text{Transmitted wave} \qquad \psi_{\text{III}}(\text{transmitted}) = Fe^{ik_{\text{I}}x} \tag{6.64c}$$

The probability of particles being reflected or transmitted is determined by the ratio of the appropriate $\psi^*\psi$. They are

$$R = \frac{|\psi_{\text{I}}(\text{reflected})|^2}{|\psi_{\text{I}}(\text{incident})|^2} = \frac{B^*B}{A^*A} \tag{6.65}$$

Probability of reflection

$$T = \frac{|\psi_{\text{III}}(\text{transmitted})|^2}{|\psi_{\text{I}}(\text{incident})|^2} = \frac{F^*F}{A^*A} \tag{6.66}$$

Probability of transmission

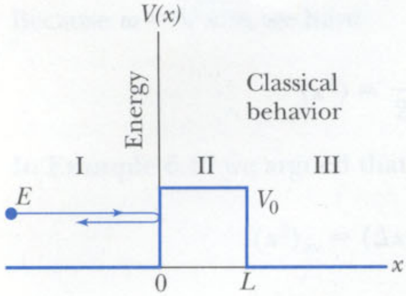


FIGURE 6.14 A particle having energy E approaches a potential barrier of height V_0 with $E < V_0$. Classically, the particle will be reflected.

where R and T are reflection and transmission probabilities, respectively. Because the particles must be either reflected or transmitted, we must have $R + T = 1$; the probability of the wave either being reflected or transmitted has to be unity.

The values of R and T are found by applying the properties(boundary conditions) of Section 6.1 as $x \to \pm\infty$, $x = 0$, and $x = L$. These conditions will result in relationships between the coefficients A, B, C, D, and F. We will not go through that tedious math here, but the result for the transmission probability is

$$T = \left(1 + \frac{V_0{}^2 \sin^2(k_{\text{II}}L)}{4E(E - V_0)}\right)^{-1} \tag{6.67}$$

Notice that there is a situation when the transmission probability is one. This occurs when $k_{\text{II}}L = n\pi$, where n is an integer. It is possible for particles moving along the $+x$ direction to be reflected both at $x = 0$ and $x = L$. Their path difference back toward the $-x$ direction is $2L$. When $2L$ equals an integral number of the wavelengths inside the potential barrier, the reflected wave functions are completely out of phase and will completely cancel.

Potential Barrier with $E < V_0$

Now we consider the situation where classically the particle does not have enough energy to surmount the potential barrier, $E < V_0$. We show the situation in Figure 6.14. In the classical situation, the particle cannot penetrate the barrier because its kinetic energy (K.E. $= E - V_0$) would be negative. The particle is reflected at $x = 0$ and returns. The quantum mechanical result, however, is one of the most remarkable features of modern physics, and there is ample experimental proof of its existence. There is a small, but finite, probability that the particle can penetrate the barrier and even emerge on the other side. Such a surprising result requires a careful inspection of the wave functions. Fortunately, there are only a few changes to the equations already presented, and they occur in region II. The wave function in region II becomes $\psi_{\text{II}} = Ce^{\kappa x} + De^{-\kappa x}$ where $\kappa = \sqrt{(2m(V_0 - E))}/\hbar$ is a positive, real number, because $V_0 > E$. The application of the boundary conditions will again relate the coefficients of the wave functions.

Tunneling

The equations for the reflection and transmission probabilities of Equations (6.65) and (6.66) are unchanged, but the results will be modified by changing $ik_{\text{II}} \to \kappa$. Quantum mechanics allows the particle to actually be on the other side of the potential barrier despite the fact that all the incident particles came in from the left moving along the $+x$ direction (see Figure 6.15). This effect is called **tunneling.** The result for the transmission probability in this case is

$$T = \left(1 + \frac{V_0{}^2 \sinh^2(\kappa L)}{4E(V_0 - E)}\right)^{-1} \tag{6.68}$$

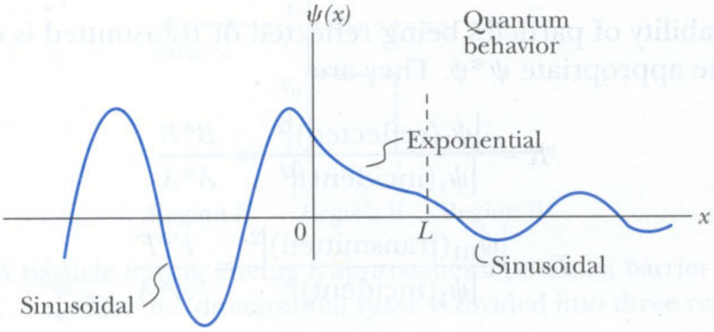


FIGURE 6.15 According to quantum mechanics, the particle approaching the potential barrier of Figure 6.14 may actually pass into the barrier and has a small probability of tunneling through the barrier and emerging at $x = L$. The particle may also be reflected at each boundary.

Note that the sine term in Equation (6.67) has been replaced by the hyperbolic sine term (sinh). When $\kappa L \gg 1$, the transmission probability equation reduces to

$$T = 16\,\frac{E}{V_0}\left(1 - \frac{E}{V_0}\right)e^{-2\kappa L} \tag{6.69}$$

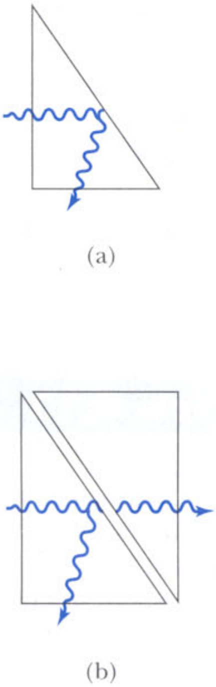
The probability of penetration is dominated by the exponentially decreasing term (although note that for a finite thickness L, the coefficient C in Equation (6.63b) is not zero). The exponential factor in Equation (6.69) depends linearly on the barrier width but only on the square root of the potential barrier height ($\kappa \sim \sqrt{V_0 - E}$). Thus, the width of the barrier is more effective than the potential height in preventing tunneling. It comes as no surprise that tunneling is observed only at the smallest distances on the atomic scale.

A simple argument based on the uncertainty principle explains tunneling. Inside the barrier region (where $0 < x < L$), the wave function ψ_{II} is dominated by the $e^{-\kappa x}$ term, and $|\psi_{\text{II}}|^2 \sim e^{-2\kappa x}$, so that over the interval $\Delta x = \kappa^{-1}$, the probability density of observing the particle has decreased markedly ($e^{-2} = 0.14$). Because $\Delta p\, \Delta x \geq \hbar$, then $\Delta p \geq \hbar/\Delta x = \hbar\kappa$. The minimum kinetic energy in this interval must be

$$\text{K.E.}_{\text{min}} = \frac{(\Delta p)^2}{2m} = \frac{\hbar^2\kappa^2}{2m} = V_0 - E$$

where we have substituted for κ in the last step. The violation allowed by the uncertainty principle (K.E.$_{\text{min}}$) is precisely equal to the *negative* kinetic energy required! The particle is allowed by quantum mechanics and the uncertainty principle to penetrate into a classically forbidden region.

Let us return briefly to our analogy with wave optics. If light passing through a glass prism reflects from an internal surface with an angle greater than the critical angle, total internal reflection occurs as seen in Figure 6.16a. However, the electromagnetic field is not totally zero just outside the prism. If we bring another prism up very close to the first one, experiment shows that the electromagnetic wave (light) appears in the second prism (see Figure 6.16b). The situation is analogous to the tunneling described here. This effect was observed by Newton and can be demonstrated with two prisms and a laser. The intensity of the second light beam decreases exponentially as the distance between the two prisms increases.*


(a)

(b)

FIGURE 6.16 (a) A light wave will be totally reflected inside a prism if the reflection angle is greater than the critical angle. (b) If a second prism is brought close to the first, there is a small probability for the wave to pass through the air gap and emerge in the second prism.

Tunneling occurs for light waves

Example 6.12

In a particular semiconductor device, electrons accelerated through a potential of 5 V attempt to tunnel through a barrier of width 0.8 nm and height 10 V. What fraction of the electrons are able to tunnel through the barrier if the potential is zero outside the barrier?

Solution: We use either Equation (6.68) or (6.69) to calculate the tunneling probability, depending on the value of κL. The energy E of the electrons is $K = 5$ eV. The potential barrier has $V_0 = 10$ eV and is zero outside the barrier.

We find the value of κ by using the mass of the electron and the appropriate energies.

$$\begin{aligned}\kappa &= \frac{\sqrt{2m(V_0 - E)}}{\hbar}\\ &= \frac{\sqrt{2(0.511 \times 10^6\ \text{eV}/c^2)(10\ \text{eV} - 5\ \text{eV})}}{6.58 \times 10^{-16}\ \text{eV}\cdot\text{s}}\\ &= \frac{3.43 \times 10^{18}\ \text{s}^{-1}}{c} = \frac{3.43 \times 10^{18}\ \text{s}^{-1}}{3 \times 10^8\ \text{m/s}} = 1.15 \times 10^{10}\ \text{m}^{-1}\end{aligned}$$

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*See D. D. Coon, *Am. J. Phys.* **34**, 240 (1966).

The value of $\kappa L = (1.15 \times 10^{10}\ \text{m}^{-1})(0.8 \times 10^{-9}\ \text{m}) = 9.2$, which might be considered to be much greater than 1, so Equation (6.69) could be used. Let's calculate the transmission probability using both equations. The approximate Equation (6.69) gives

$$T = 16\left(\frac{5\ \text{eV}}{10\ \text{eV}}\right)\left(1 - \frac{5\ \text{eV}}{10\ \text{eV}}\right)e^{-18.4} = 4.1 \times 10^{-8}$$

The more accurate Equation (6.68) gives

$$T = \left(\frac{1 + (10\ \text{eV})^2 \sinh^2(9.2)}{4(5\ \text{eV})(5\ \text{eV})}\right)^{-1} = 4.1 \times 10^{-8}$$

The approximate equation, valid when $\kappa L \gg 1$, works well in this case.

Example 6.13

Consider a particle of kinetic energy E approaching the step function of Figure 6.17 from the left, where the potential barrier steps from 0 to V_0 at $x = 0$. Find the penetration distance Δx, where the probability of the particle penetrating into the barrier drops to $1/e$. Calculate the penetration distance for a 5-eV electron approaching a step barrier of 10 eV.

Solution: We can use the results of this section to find the wave functions in the two regions $x < 0$ and $x > 0$.

$$\psi_{\text{I}} = Ae^{ikx} + Be^{-ikx} \qquad x < 0$$

$$\psi_{\text{II}} = Ce^{\kappa x} + De^{-\kappa x} \qquad x > 0$$

where

$$k = \frac{\sqrt{2mE}}{\hbar}$$

$$\kappa = \frac{\sqrt{2m(V_0 - E)}}{\hbar}$$

Because the wave function ψ_{II} must go to zero when $x \to \infty$, the coefficient $C = 0$, so we have

$$\psi_{\text{II}} = De^{-\kappa x} \qquad x > 0$$

The probability distribution for $x > 0$ is $|\psi_{\text{II}}|^2$. The probability has dropped to e^{-1} for the penetration distance Δx, so we have

$$e^{-1} = \frac{\psi_{\text{II}}{}^2(x = \Delta x)}{\psi_{\text{II}}{}^2(x = 0)} = e^{-2\kappa\Delta x}$$

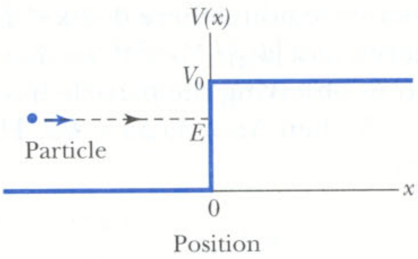

FIGURE 6.17 A particle of energy E approaches a potential barrier from the left. The step potential is $V = 0$ for $x < 0$ and $V = V_0$ for $x > 0$.

From this equation we have $1 = 2\kappa\Delta x$, and the penetration distance becomes

$$\Delta x = \frac{1}{2\kappa} = \frac{\hbar}{2\sqrt{2m(V_0 - E)}}$$

This is the result we needed.

Now we find the penetration distance for the 5-eV electron.

$$\Delta x = \frac{\hbar c}{2\sqrt{2mc^2(V_0 - E)}}$$

$$= \frac{197.3\ \text{eV} \cdot \text{nm}}{2\sqrt{2(0.511 \times 10^6\ \text{eV})(10\ \text{eV} - 5\ \text{eV})}} = 0.044\ \text{nm}$$

Electrons do not penetrate very far into the classically forbidden region.

Potential Well

Consider a particle of energy $E > 0$ passing through the potential well region (Figure 6.18), rather than a potential barrier. Let $V = -V_0$ in the region $0 < x < L$ and zero elsewhere. Classically, the particle would speed up passing the well region, because $mv^2/2 = E + V_0$. According to quantum mechanics, reflection and transmission may occur, but the wavelength inside the potential well is smaller than outside. When the width of the potential well is precisely equal to

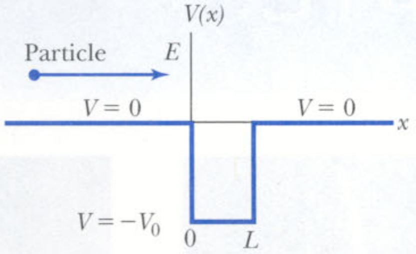

FIGURE 6.18 A particle of energy E approaches a potential well from the left. The potential is $V = 0$ everywhere except between $0 < x < L$, where $V = -V_0$.

half-integral or integral units of the wavelength, the reflected waves may be out of phase or in phase with the original wave, and cancellations or resonances may occur. The reflection/cancellation effects can lead to almost pure transmission or pure reflection for certain wavelengths. For example, at the second boundary ($x = L$) for a wave passing to the right, the wave may reflect and be out of phase with the incident wave. The effect would be a cancellation inside the well.

Alpha-Particle Decay

The phenomenon of tunneling explains the alpha-particle decay of heavy, radioactive nuclei. Many nuclei heavier than lead are natural emitters of alpha particles, but their emission rates vary over a factor of 10^{13}, whereas their energies tend to range only from 4 to 8 MeV. Inside the nucleus, an alpha particle feels the strong, short-range attractive nuclear force as well as the repulsive Coulomb force. The shape of the potential well is shown in Figure 6.19. The nuclear force dominates inside the nuclear radius r_N, and the potential can be approximated by a square well. However, outside the nucleus, the Coulomb force dominates. The so-called Coulomb potential energy barrier of Figure 6.19 can be several times the typical kinetic energy $E(\sim 5 \text{ MeV})$ of an alpha particle.

The alpha particle therefore is trapped inside the nucleus. Classically, it does not have enough energy to surmount the Coulomb potential barrier. According to quantum mechanics, however, the alpha particle can "tunnel" through the barrier. The widely varying rates of alpha emission from radioactive nuclei can be explained by small changes in the potential barrier (both height and width). A small change in the barrier can manifest itself greatly in the transmission probability, because of the exponential behavior in $e^{-2\kappa L}$.

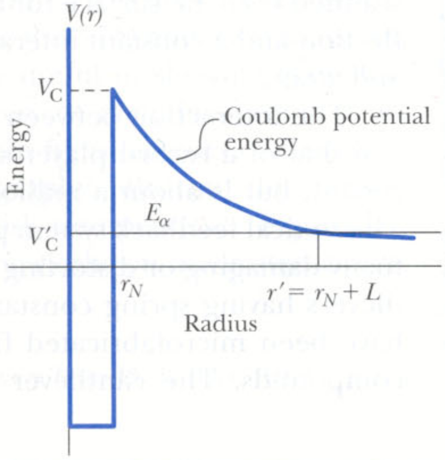

FIGURE 6.19 An α particle of energy E_α is trapped inside a heavy nucleus by the large nuclear potential. Classically, it can never escape, but quantum mechanically it may tunnel through and escape.

SPECIAL TOPIC:

SCANNING PROBE MICROSCOPES

Scanning probe microscopes, consisting at present of two types, **scanning tunneling microscopes** (STM) and **atomic force microscopes** (AFM), have revolutionized the imaging of atomic surfaces. Gerd Binnig and Heinrich Rohrer (Nobel Prize, 1986) invented the STM in the early 1980s at the IBM Research Laboratory in Zürich, Switzerland. Later in 1985 while Binnig was on leave at Stanford University and IBM's Almaden Research Center, he thought up the concept of the AFM which he developed with Christoph Gerber of IBM and Calvin Quate of Stanford.

In the most common form of the STM a constant bias voltage of appropriate polarity is applied between the atoms of a tip and the sample to be examined (see Figure A). Electrons tunnel across this gap, and the sensitivity of the tunneling current to the gap distance is the key to the STM capability. The tunneling current can be as small as a few pA (10^{-12} A), and a change in the tunneling gap of only 0.4 nm can cause a factor of 10^4 in the tunneling current. In order to keep the tunneling current constant, a feedback system based on the current causes the tip to be moved up and down tracing out the contours of the sample atoms. The path of the tip is shown by the solid black line in Figure A. There are variations to this method.

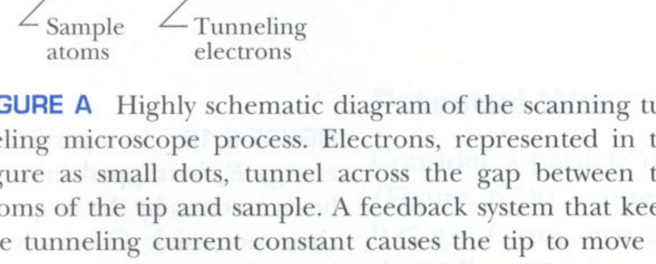

FIGURE A Highly schematic diagram of the scanning tunneling microscope process. Electrons, represented in the figure as small dots, tunnel across the gap between the atoms of the tip and sample. A feedback system that keeps the tunneling current constant causes the tip to move up and down tracing out the contours of the sample atoms.

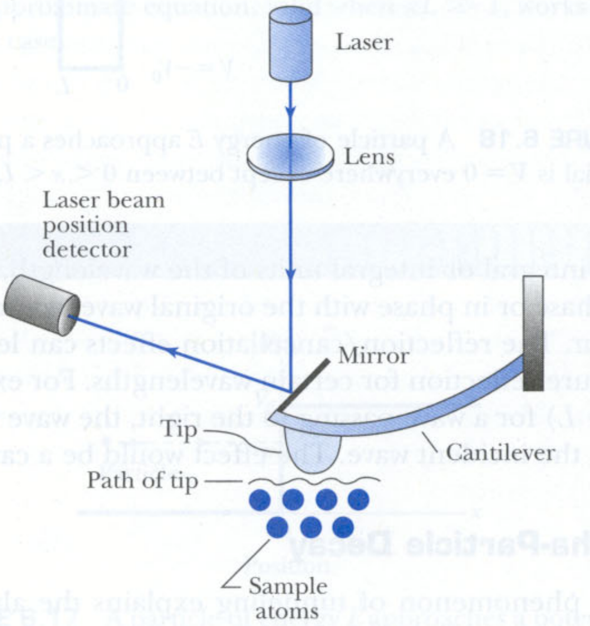

FIGURE B Highly schematic diagram of the atomic force microscope. A feedback signal from the detection of the laser beam reflecting off the mirror that is mounted on the cantilever provides a signal to move the sample atoms up or down to keep the cantilever force constant. The movement of the sample atoms traces out the contours of the sample atoms.

The AFM depends on the interatomic forces between the tip and sample atoms as shown in Figure B. In some systems, the sample atoms are scanned horizontally while the sample is moved up and down to keep the force between the tip and sample atoms constant. The interatomic forces cause the very sensitive cantilever to bend. By reflecting a laser off the end of the cantilever arm into an optical sensor, the feedback signal from this sensor controls the sample height, giving the topography of the atomic surface. The tip is scanned over the surface for a constant cantilever deflection and a constant interatomic force between tip and atom.

The interaction between tip and sample is much like that of a record player stylus moving across the record, but is about a million times more sensitive. The optical feedback system prevents the tip from actually damaging or distorting the sample atoms. Cantilevers having spring constants as small as 0.1 N/m have been microfabricated from silicon and silicon compounds. The cantilever lateral dimensions are

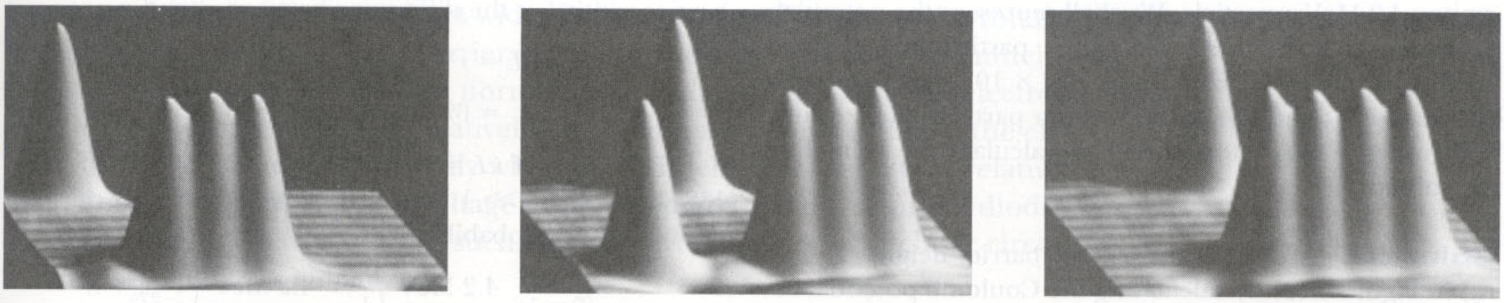

FIGURE C These three photos, taken with a STM, show xenon atoms placed on a nickel surface. The xenon atoms are 0.16 nm high and adjacent xenon atoms are 0.5 nm apart (the vertical scale has been exaggerated). The small force between the STM tip and an atom is enough to drag one xenon atom at a time across the nickel. The nickel atoms are represented by the black and white stripes on the horizontal surface. See also Figure 1.7. The image is magnified about 5 million times. *Courtesy of International Business Machines.*

on the order of 100 μm with thicknesses of about 1 μm. In comparison the spring constant of a piece of household aluminum foil 4 mm by 1 mm is about 1 N/m. The tapered tips may have an end dimension of only 50 nm. The tracking forces felt by the cantilever can be as small as 10^{-9} N. Daniel Rugar and Paul Hansma have written an excellent description of the AFM.*

The primary disadvantage of the STM compared to the AFM is that a conducting surface is required for the STM. This limits the applications of the STM, because either conductors must be scanned or a thin conductive metal coating must be placed on the sample. Because the AFM works for both insulators and conductors, it can be used for ceramics, polymers, optical surfaces, and biological structures. We showed in Figure 1.7 a photo indicating individual atoms taken using an STM. Those atoms can be individually moved as shown in Figure C. It is not only individual atomic images that make the STM and AFM so useful. They are perhaps more useful in showing gross features such as the flatness of materials, grain structures, the breakup of thin films, magnetic bit shapes, integrated circuit topography, lubricant thicknesses, inspection of optical disk stampers (see Figure D), and measurement of linewidths on integrated circuit masks. Biological applications of AFM include the imaging of amino acids, DNA, proteins and even leaf sections from a perennial cranberry vine. The AFM has been used to observe the polymerization of blood clotting protein fibrin. Real-time imaging of biological samples offers incredible possibilities, for example, the attachment of the AIDS virus onto cell membranes. Both STM and AFM instruments are now commercially available, and new variations are being developed.

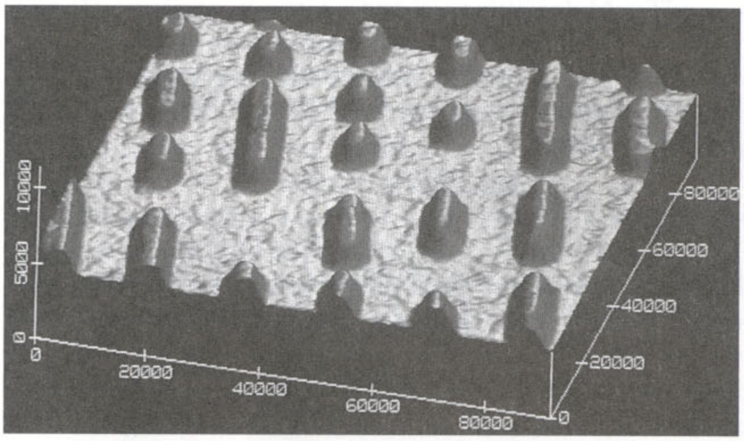

FIGURE D An atomic force microscope scan of a stamper used to mold compact disks. The numbers given are in nm. The bumps on this metallic mold stamp out 60-nm-deep holes in tracks that are 1.6 μm apart in the optical disks. *Photo courtesy of Digital Instruments/Veeco Metrology Group, Santa Barbara, CA.*

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*D. Rugar and P. Hansma, *Physics Today* **43**, 23 (Oct. 1990).

Example 6.14

Consider the α-particle emission from a ^{238}U nucleus, which emits a 4.2-MeV α particle. We shall represent the potentials as displayed in Figure 6.19. The α particle is contained inside the nuclear radius of $r_N \approx 7 \times 10^{-15}$ m. Find the barrier height and the distance the α particle must tunnel, and, using a square-top potential, calculate the tunneling probability.

Solution: We shall calculate the barrier height ($V_C(r = r_N)$ in Figure 6.19) by calculating the Coulomb potential between an α particle and the remainder of the uranium nucleus for a separation of the nuclear radius, 7×10^{-15} m.

$$V_C = \frac{Z_1 Z_2 e^2}{4\pi\epsilon_0 r_N}$$

$$= \frac{2(90)(1.6 \times 10^{-19}\ \mathrm{C})^2(9 \times 10^9\ \mathrm{N \cdot m^2/C^2})}{7 \times 10^{-15}\ \mathrm{m}} \times \left(\frac{10^{-6}\ \mathrm{MeV}}{1.6 \times 10^{-19}\ \mathrm{J}}\right)$$

$$= 37\ \mathrm{MeV}$$

We determine the distance r' through which the α particle must tunnel by setting K.E. $= V_C(r = r')$ at that distance (see Figure 6.19). Because the K.E. = 4.2 MeV, we have

$$4.2\ \mathrm{MeV} = \frac{Z_1 Z_2 e^2}{4\pi\epsilon_0 r'}$$

We solve this equation for r' which yields

$$r' = \frac{37\ \mathrm{MeV}}{4.2\ \mathrm{MeV}} r_N = 6.2 \times 10^{-14}\ \mathrm{m} = 62\ \mathrm{fm}$$

where we have used the result above for V_C and r_N.

We make a simple, but rough, approximation of a square-top potential where $V = 37$ MeV for 7 fm $< r <$ 62 fm. We then find

$$\kappa = \frac{\sqrt{2m(V - E)}}{\hbar}$$

$$= \frac{\sqrt{2(3727\ \mathrm{MeV}/c^2)(37\ \mathrm{MeV} - 4.2\ \mathrm{MeV})}}{6.58 \times 10^{-22}\ \mathrm{MeV \cdot s}}$$

$$= 2.5 \times 10^{15}\ \mathrm{m}^{-1}$$

where the mass of the alpha particle is 3727 MeV/c^2. The barrier width L is the difference between r' and r_N.

$$L = r' - r_N$$

$$= 62\ \mathrm{fm} - 7\ \mathrm{fm} = 55\ \mathrm{fm}$$

The value of $\kappa L = (2.5 \times 10^{15}\ \mathrm{m}^{-1})(55 \times 10^{-15}\ \mathrm{m}) = 138$. Because $kL \gg 1$, we use Equation (6.69) to calculate the tunneling probability.

$$T = 16\,\frac{4.2\ \mathrm{MeV}}{37\ \mathrm{MeV}}\left(1 - \frac{4.2\ \mathrm{MeV}}{38\ \mathrm{MeV}}\right)e^{-275}$$

$$= 1.6e^{-275} = 6 \times 10^{-120}$$

which is an extremely small number.

Our assumption of a square-top potential of the full height and full width is very unrealistic. A closer approximation to the potential shown in Figure 6.19 would be a square-top potential of only half the maximum Coulomb potential (18 MeV rather than 37 MeV) and a barrier width of only half L (28 fm rather than 55 fm). If we use 18 MeV in the calculation of κ we obtain $1.7 \times 10^{15}\ \mathrm{m}^{-1}$. The tunneling probability now becomes

$$T = 16\,\frac{4.2\ \mathrm{MeV}}{18\ \mathrm{MeV}}\left(1 - \frac{4.2\ \mathrm{MeV}}{18\ \mathrm{MeV}}\right) \times \exp[-2(1.7 \times 10^{15}\ \mathrm{m}^{-1})(2.8 \times 10^{-14}\ \mathrm{m})]$$

$$= 2.9\ e^{-95} = 1.6 \times 10^{-41}$$

This still seems like a very low probability, but let us see if we can determine how long it takes the α particle to tunnel out. If the α particle has a kinetic energy of 4.2 MeV, its velocity is determined nonrelativistically by

$$\mathrm{K.E.} = \frac{1}{2}mv^2$$

$$v = \sqrt{\frac{2\,\mathrm{K.E.}}{m}} = \sqrt{\frac{2(4.2\ \mathrm{MeV})}{3727\ \mathrm{MeV}/c^2}} = 0.047c = 1.4 \times 10^7\ \mathrm{m/s}$$

The diameter of the nucleus is about 1.4×10^{-14} m, so it takes the α particle $1.4 \times 10^{-14}\ \mathrm{m}/(1.4 \times 10^7\ \mathrm{m/s}) \approx 10^{-21}$ s to cross. The α particle must make many traverses back and forth across the nucleus before it can escape. According to our probability it must make about 10^{41} attempts, so we estimate the α particle may tunnel through in about 10^{20} s. The half-life of a ^{238}U nucleus is 4.5×10^9 yr or about 10^{17} s. Our rough estimate does not seem all that bad.

Tunnel Diode. An extremely useful application of tunneling is that of a tunnel diode, which is a special kind of semiconductor. In a tunnel diode, electrons may pass from one region through a junction into another region. We can depict the behavior by considering a potential barrier over the region of the junction, which may be only 10 nm wide. Both positive and negative bias voltages may be applied to change the barrier height to allow the electrons to tunnel either way through the barrier. In a normal semiconductor junction, the electrons (and holes) diffuse through, a relatively slow process. In a tunnel diode, the electrons tunnel through quite rapidly when the tunneling probability is relatively high. Because the applied bias voltage can be changed rapidly, a tunnel diode is an extremely fast device and, as such, has important uses in switching circuits and high-frequency oscillators.

Summary

Werner Heisenberg and Erwin Schrödinger developed modern quantum theory in the 1920s. The time-dependent Schrödinger wave equation for the wave function $\Psi(x, t)$ is expressed as

$$i\hbar \frac{\partial \Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi(x,t)}{\partial x^2} + V\Psi(x,t) \qquad (6.1)$$

The time-independent form for the spatial dependence (in one dimension) of $\psi(x)$, where $\Psi(x, t) = \psi(x)e^{-iEt/\hbar}$, is

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

Certain properties of Ψ and $\partial\Psi/\partial x$ lead to quantized behavior. The wave function $\Psi(x, t)$ must be finite, single valued, and continuous; $\partial\Psi/\partial x$ must be continuous. The wave function must be normalized in order to use it to determine probabilities.

Average values of the physical observables are determined by calculating the expectation values using the wave functions. The expectation value of a function $g(x)$ is found from

$$\langle g(x)\rangle = \int_{-\infty}^{\infty} \Psi^*(x,t)g(x)\Psi(x,t)\,dx \qquad (6.20)$$

To find the expectation values of the momentum and energy, we need to know the appropriate operators. In these two cases the operators are

$$\hat{p} = -i\hbar\frac{\partial}{\partial x} \qquad (6.21)$$

$$\hat{E} = i\hbar\frac{\partial}{\partial t} \qquad (6.25)$$

and the expectation values $\langle p\rangle$ and $\langle E\rangle$ are

$$\langle p\rangle = -i\hbar\int_{-\infty}^{\infty} \Psi^*(x,t)\frac{\partial\Psi(x,t)}{\partial x}\,dx \qquad (6.23)$$

$$\langle E\rangle = i\hbar\int_{-\infty}^{\infty} \Psi^*(x,t)\frac{\partial\Psi(x,t)}{\partial t}\,dx \qquad (6.26)$$

The infinite square-well potential is a particularly simple application of the Schrödinger wave equation, and it leads to quantized energy levels and quantum numbers. The three-dimensional infinite square-well potential leads to the concept of degeneracy, different physical states with the same energy.

The simple harmonic oscillator, where the potential is $V(x) = \kappa x^2/2$, is an important application of the Schrödinger wave equation because it approximates many complex systems in nature but is exactly soluble. The energy levels of the simple harmonic oscillator are $E_n = (n + 1/2)\hbar\omega$, where $n = 0$ represents the ground state energy $E_0 = \hbar\omega/2$. The fact that the minimum energy is not zero—that the oscillator exhibits zero-point motion—is a consequence of the uncertainty principle.

Finite potentials lead to the possibility of a particle entering a region that is classically forbidden, where $V_0 > E$ (negative kinetic energy). This quantum process is called *tunneling* and is studied by considering various potential barrier shapes. Important examples of quantum tunneling are alpha decay and tunnel diodes. Tunneling is consistent with the uncertainty principle and occurs only for short distances.

Questions

1. Why can we use the nonrelativistic form of the kinetic energy in treating the structure of the hydrogen atom?
2. How do you reconcile the fact that the probability density for the ground state of the quantum harmonic oscillator (Figure 6.10c) has its peak at the center and its minima at its ends, while the classical harmonic oscillator's probability density (Figure 6.11) has a minimum at the center and peaks at each end? If you do this experiment with an actual mass and spring, what experimental result for its position distribution would you expect to obtain? Why?
3. Notice for the finite square-well potential that the wave function ψ is not zero outside the well despite the fact that $E < V_0$. Is it possible classically for a particle to be in a region where $E < V_0$? Explain this result.
4. In a given tunnel diode the *p-n* junction width is fixed. How can we change the time response of the tunnel diode most easily? Explain.
5. A particle in a box has a first excited state that is 3 eV above its ground state. What does that tell you about the box?
6. Does the wavelength of a particle change after it tunnels through a barrier as shown in Figure 6.15? Explain.
7. Can a particle be observed while it is tunneling through a barrier? What would its wavelength, momentum, and kinetic energy be while it tunnels through the barrier?
8. Is it easier for an electron or a proton of the same energy to tunnel through a given potential barrier? Explain.
9. Can a wave packet be formed from a superposition of wave functions of the type $e^{i(kx - \omega t)}$? Can it be normalized?
10. Given a particular potential V and wave function Ψ, how could you prove that the given Ψ is correct? Could you determine an appropriate E if the potential is independent of time?
11. Compare the infinite square-well potential with the finite one. Where is the Schrödinger wave equation the same? Where is it different?
12. Tunneling can occur for an electron trying to pass through a very thin tunnel diode. Can a baseball tunnel through a very thin window? Explain.
13. For the three-dimensional cubical box, the ground state is given by $n_1 = n_2 = n_3 = 1$. Why is it not possible to have one $n_i = 1$ and the other two equal to zero?

Problems

6.1 The Schrödinger Wave Equation

1. Try to normalize the wave function $e^{i(kx - \omega t)}$. Why can't it be done over all space? Explain why it is not possible.
2. (a) In what direction does a wave of the form $A\sin(kx - \omega t)$ move? (b) What about $B\sin(kx + \omega t)$? (c) Is $e^{i(kx-\omega t)}$ a real number? (d) In what direction is the wave in (c) moving? Explain.
3. Show directly that the trial wave function $\Psi(x, t) = Ae^{i(kx-\omega t)}$ satisfies Equation (6.1).
4. Normalize the wave function $Ae^{i(kx-\omega t)}$ in the region $x = 0$ to a.
5. Normalize the wave function $Are^{-r/\alpha}$ from $r = 0$ to ∞ where α and A are constants.
6. Property (2) specifies that Ψ must be continuous in order to avoid discontinuous probability values. Why can't we have such probabilities?
7. Consider the wave function $Ae^{-\alpha|x|}$ that we used in Example 6.4. (a) How does this wave function satisfy the boundary conditions of Section 6.1? (b) What can we conclude about this wave function? (c) If the wave function is unacceptable as is, how could it be fixed?

6.2 Expectation Values

8. A set of measurements has given the following result for the measurement of x (in some units of length): 3.4, 3.9, 5.2, 4.7, 4.1, 3.8, 3.9, 4.7, 4.1, 4.5, 3.8, 4.5, 4.8, 3.9, and 4.4. Find the average value of x, called $\bar{x}$ or $\langle x \rangle$, and average value of x^2, called $\langle x^2 \rangle$. Show that the standard deviation of x, given by

$$\sigma = \sqrt{\frac{\sum (x_i - \bar{x})^2}{N}}$$

where x_i is the individual measurement and N is the number of measurements, is also given by $\sigma = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$. Find the value of σ for the set of data.

If the potential V is independent of time, show that the expectation value for x is independent of time.

A wave function $\psi = A(e^{ix} + e^{-ix})$ in the region $-\pi < x < \pi$ and zero elsewhere. Normalize the wave function and find the probability of the particle being between $x = 0$ and $\pi/8$.

A wave function has the value $A \sin x$ between 0 and π, but zero elsewhere. Normalize the wave function and find the probability that the particle is between $x = 0$ and $\pi/4$.

Infinite Square-Well Potential

Find an equation for the difference between adjacent energy levels ($\Delta E_n = E_{n+1} - E_n$) for the infinite square-well potential. Calculate ΔE_1, ΔE_8, and ΔE_{800}.

Determine the average value of $\psi_n^2(x)$ inside the well for the infinite square-well potential for $n = 1, 5, 20$, and 100. Compare these averages with the classical probability of detecting the particle inside the box.

An electron moves with a speed $v = 10^{-4}c$ inside a one-dimensional box ($V = 0$) of length 48.5 nm. The potential is infinite elsewhere. The particle may not escape the box. What approximate quantum number does the electron have?

For the infinite square-well potential, find the probability that a particle in its ground state is in each third of the one-dimensional box: $0 \le x \le L/3$, $L/3 \le x \le 2L/3$, $2L/3 \le x \le L$.

Repeat the previous problem using the first excited state.

Repeat Example 6.8 for an electron inside the nucleus. Assume nonrelativistic equations and find the transition energy for an electron. (See Example 6.8 for an interpretation of the result.)

What is the minimum energy of (a) a proton and (b) an α particle trapped in a one-dimensional region the size of a uranium nucleus (radius $= 7 \times 10^{-15}$ m)?

An electron is trapped in an infinite square-well potential of width 0.5 nm. If the electron is initially in the $n = 4$ state, what are the various photon energies that can be emitted as the electron jumps to the ground state?

Finite Square-Well Potential

Consider a finite square-well potential well of width 3×10^{-15} m that contains a particle of mass 2 GeV/c^2. How deep does this potential well need to be to contain three energy levels? (Except for the energy levels, this situation approximates a deuteron.)

Compare the results of the infinite and finite square-well potentials. (a) Are the wavelengths longer or shorter for the finite square well compared with the infinite well? (b) Using physical arguments, do you expect the energies (for a given quantum number n) to be (i) larger or (ii) smaller for the finite square well than for the infinite square well? (c) Why will there be a finite number of bound energy states for the finite potential?

22. Apply the boundary conditions to the finite square-well potential at $x = 0$ to find the relationships between the coefficients A, C, and D and the ratio C/D.

23. Apply the boundary conditions to the finite square-well potential at $x = L$ to find the relationship between the coefficients B, C, and D and the ratio C/D.

6.5 Three-Dimensional Infinite-Potential Well

24. Find the energies of the second, third, fourth, and fifth levels for the three-dimensional cubical box. Which are degenerate?

25. Write the possible (unnormalized) wave functions for each of the first four excited energy levels for the cubical box.

26. Find the normalization constant A for the ground state wave function for the cubical box in Equation (6.52).

27. Complete the derivation of Equation (6.49) by substituting the wave function given in Equation (6.47) into Equation (6.46). What is the origin of the three quantum numbers?

6.6 Simple Harmonic Oscillator

28. In Figure 6.9 we showed a plausible guess for the wave function ψ_0 for the lowest energy level E_0 of the simple harmonic oscillator. Explain the shape of the wave function and explain why it is a maximum at $x = 0$ and not zero when $E = V_0$.

29. What is the energy level difference between adjacent levels $\Delta E_n = E_{n+1} - E_n$ for the simple harmonic oscillator? What is ΔE_0, ΔE_2, and ΔE_{50}? How many possible energy levels are there?

30. The wave function for the first excited state ψ_1 for the simple harmonic oscillator is $\psi_1 = Axe^{-\alpha x^2/2}$. Normalize the wave function to find the value of the constant A. Determine $\langle x \rangle$, $\langle x^2 \rangle$, and $\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$.

31. An atom of mass 3.32×10^{-26} kg oscillates in one dimension at a frequency of 10^{13} Hz. What are its effective force constant and quantized energy levels?

32. One possible solution for the wave function ψ_n for the simple harmonic oscillator is

$$\psi_n = A(2\alpha x^2 - 1)e^{-\alpha x^2/2}$$

where A is a constant. What is the value of the energy level E_n?

33. What would you expect for $\langle p \rangle$ and $\langle p^2 \rangle$ for the ground state of the simple harmonic oscillator? (*Hint:* Use symmetry and energy arguments.)

34. Show that the energy of a simple harmonic oscillator in the $n = 1$ state is $3\,\hbar\omega/2$ by substituting the wave function $\psi_1 = Axe^{-\alpha x^2/2}$ directly into the Schrödinger equation.

35. A H_2 molecule can be approximated by a simple harmonic oscillator having spring constant $k = 1.1 \times 10^3$ N/m. Find (a) the energy levels, and (b) the possible wavelengths of photons emitted when the H_2 molecule decays from the third excited state eventually to the ground state.

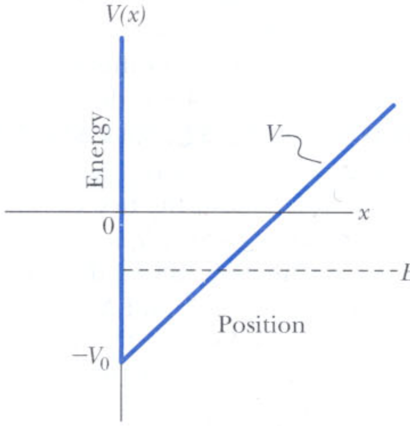
6.7 Barriers and Tunneling

36. The creation of elements in the early universe and in stars involves protons tunneling into nuclei. Find the probability of the proton tunneling through ^{12}C. Let the proton and carbon be inside a star of temperature 12,000 K.

37. Compare the wavelength of a particle when it passes a barrier of height (a) $+V_0$ (see Figure 6.12) and (b) $-V_0$ where $E > |V_0|$ (see Figure 6.18). Calculate the momentum and kinetic energy for both cases.

38. (a) Calculate the transmission probability of an α particle of energy $E = 5$ MeV through a Coulomb barrier of a heavy nucleus that is approximated by a square barrier with $V_0 = 15$ MeV and barrier width $L = 1.3 \times 10^{-14}$ m. Calculate the probability (b) by doubling the potential barrier height and (c) by using the original barrier height but doubling the barrier width. Compare all three probabilities.

39. Consider a particle of energy E trapped inside the potential well shown in the accompanying figure. Sketch a possible wave function inside and outside the potential well. Explain your sketch.



A potential well is infinite for $x < 0$ but increases linearly from $V = -V_0$ at $x = 0$.

40. When a particle of energy E approaches a potential barrier of height V_0, where $E \gg V_0$, show that the reflection coefficient is about $((V_0 \sin(kL))/2E)^2$.

41. Let 11.0-eV electrons approach a potential barrier of height 3.8 eV. (a) For what barrier thickness is there no reflection? (b) For what barrier thickness is the reflection a maximum?

42. A 1-eV electron has a 10^{-4} probability of tunneling through a 2.5-eV potential barrier. What is the probability of a 1-eV proton tunneling through the same barrier?

General Problems

43. A particle of mass m is trapped in a three-dimensional rectangular potential well with sides of length L, $L/\sqrt{2}$, and $2L$. Inside the box $V = 0$, outside $V = \infty$. Assume

$$\psi = A \sin(k_1 x) \sin(k_2 y) \sin(k_3 z)$$

inside the well. Substitute this ψ into the Schrödinger equation and apply appropriate boundary conditions to find the allowed energy levels. Find the energy of the ground and first four excited levels. Which of these levels are degenerate?

44. For a region where the potential $V = 0$, the wave function is given by $\sqrt{2/\alpha}\,\sin(3\pi x/\alpha)$. Calculate the energy of this system.

45. Consider the semi-infinite-well potential in which $V = \infty$ for $x \leq 0$, $V = 0$ for $0 < x < L$, and $V = V_0$ for $x > L$. (a) Show that possible wave functions are $A \sin k_n x$ inside the well and $Be^{-\kappa_n x}$ for $x > L$, where $k_n = \sqrt{2mE_n}/\hbar$ and $\kappa_n = \sqrt{2m(V_0 - E)}/\hbar$. (b) Show that the application of the boundary conditions gives $\kappa \tan(kL) = -k$.

46. Assume that $V_0 = \hbar^2/2mL^2$ and show that the ground state energy of a particle in the semi-infinite well of the previous problem is given by $0.04\hbar^2/2mL^2$.

47. Prove that there are a limited number of bound solutions for the semi-infinite well.

48. Use the semi-infinite-well potential to model a deuteron, a nucleus consisting of a neutron and a proton. Let the well width be 3.5×10^{-15} m and $V_0 - E = 2.2$ MeV. Determine the energy E. How many excited states are there, and what are their energies?

49. The wave function for the $n = 2$ state of a simple harmonic oscillator is $A(1 - 2\alpha x^2)e^{-\alpha x^2/2}$. (a) Show that its energy level is $5\,\hbar\omega/2$ by substituting the wave function into the Schrödinger equation. (b) Find $\langle x \rangle$ and $\langle x^2 \rangle$.

50. A particle is trapped inside an infinite square-well potential between $x = 0$ and $x = L$. Its wave function is a superposition of the ground state and first excited state. Its wave function is given by

$$\Psi(x) = \frac{1}{2}\Psi_1(x) + \frac{\sqrt{3}}{2}\Psi_2(x)$$

Show that the wave function is normalized.

51. The *Morse potential* is a good approximation for a real potential to describe diatomic molecules. It is given by $V(r) = D(1 - e^{-a(r-r_e)})^2$ where D is the molecular dissociation energy, and r_e is the equilibrium distance between the atoms. For small vibrations, $r - r_e$ is small, and $V(r)$ can be expanded in a Taylor series to reduce to a simple harmonic potential. Find the lowest term of $V(r)$ in this expansion and show that it is quadratic in $(r - r_e)$.

52. Show that the vibrational energy levels E_v for the *Morse potential* of the previous problem are given by

$$E_v = \hbar\omega\left(n + \frac{1}{2}\right) - \frac{\hbar^2\omega^2}{4D}\left(n + \frac{1}{2}\right)^2$$

where $$\omega = a\sqrt{\frac{2D}{m_r}}$$

and n is the vibrational quantum number, m_r is the reduced mass, and $E_v \ll D$. Find the three lowest energy levels for KCl where $D = 4.42$ eV, and $a = 7.8\ \mathrm{nm}^{-1}$.

53. Consider a particle of mass m trapped inside a two-dimensional square box of sides L aligned along the x and y axes. Show that the wave function and energy levels are given by

$$\psi(x, y) = \frac{2}{L}\sin\frac{n_x\pi x}{L}\sin\frac{n_y\pi y}{L}$$

$$E = \frac{\hbar^2\pi^2}{2mL^2}(n_x^2 + n_y^2)$$

Plot the first six energy levels and give their quantum numbers.