

5.1 QUANTUM MECHANICS

Classical mechanics is an approximation of quantum mechanics

The fundamental difference between classical (or newtonian) mechanics and quantum mechanics lies in what they describe. In classical mechanics, the future history of a particle is completely determined by its initial position and momentum together with the forces that act upon it. In the everyday world these quantities can all be determined well enough for the predictions of newtonian mechanics to agree with what we find.

Quantum mechanics also arrives at relationships between observable quantities, but the uncertainty principle suggests that the nature of an observable quantity is different in the atomic realm. Cause and effect are still related in quantum mechanics, but what they concern needs careful interpretation. In quantum mechanics the kind of certainty about the future characteristic of classical mechanics is impossible because the initial state of a particle cannot be established with sufficient accuracy. As we saw in Sec. 3.7, the more we know about the position of a particle now, the less we know about its momentum and hence about its position later.

The quantities whose relationships quantum mechanics explores are *probabilities*. Instead of asserting, for example, that the radius of the electron's orbit in a ground-state hydrogen atom is always exactly 5.3×10^{-11} m, as the Bohr theory does, quantum mechanics states that this is the *most probable* radius. In a suitable experiment most trials will yield a different value, either larger or smaller, but the value most likely to be found will be 5.3×10^{-11} m.

Quantum mechanics might seem a poor substitute for classical mechanics. However, classical mechanics turns out to be just an approximate version of quantum mechanics. The certainties of classical mechanics are illusory, and their apparent agreement with experiment occurs because ordinary objects consist of so many individual atoms that departures from average behavior are unnoticeable. Instead of two sets of physical principles, one for the macroworld and one for the microworld, there is only the single set included in quantum mechanics.

Wave Function

As mentioned in Chap. 3, the quantity with which quantum mechanics is concerned is the **wave function** Ψ of a body. While Ψ itself has no physical interpretation, the square of its absolute magnitude $|\Psi|^2$ evaluated at a particular place at a particular time is proportional to the probability of finding the body there at that time. The linear momentum, angular momentum, and energy of the body are other quantities that can be established from Ψ . The problem of quantum mechanics is to determine Ψ for a body when its freedom of motion is limited by the action of external forces.

Wave functions are usually complex with both real and imaginary parts. A probability, however, must be a positive real quantity. The probability density $|\Psi|^2$ for a complex Ψ is therefore taken as the product $\Psi^*\Psi$ of Ψ and its **complex conjugate** Ψ^* . The complex conjugate of any function is obtained by replacing i ($=\sqrt{-1}$) by $-i$ wherever it appears in the function. Every complex function Ψ can be written in the form

Wave function

$$\Psi = A + iB$$

where A and B are real functions. The complex conjugate Ψ^* of Ψ is

Complex conjugate

$$\Psi^* = A - iB$$

and so

$$\Psi^*\Psi = A^2 - i^2B^2 = A^2 + B^2$$

since $i^2 = -1$. Hence $\Psi^*\Psi$ is always a positive real quantity, as required.

Even before we consider the actual calculation of Ψ , we can establish certain requirements it must always fulfill. For one thing, since $|\Psi|^2$ is proportional to the probability density P of finding the body described by Ψ , the integral of $|\Psi|^2$ over all space must be finite—the body is *somewhere*, after all. If

$$\int_{-\infty}^{\infty} |\Psi|^2 dV = 0$$

the particle does not exist, and the integral obviously cannot be ∞ and still mean anything. Furthermore, $|\Psi|^2$ cannot be negative or complex because of the way it is defined. The only possibility left is that the integral be a finite quantity if Ψ is to describe properly a real body.

It is usually convenient to have $|\Psi|^2$ be *equal* to the probability density P of finding the particle described by Ψ , rather than merely be proportional to P . If $|\Psi|^2$ is to equal P , then it must be true that

Normalization

$$\int_{-\infty}^{\infty} |\Psi|^2 dV = 1 \tag{5.1}$$

since if the particle exists somewhere at all times,

$$\int_{-\infty}^{\infty} P dV = 1$$

A wave function that obeys Eq. (5.1) is said to be **normalized**. Every acceptable wave function can be normalized by multiplying it by an appropriate constant; we shall shortly see how this is done.

Besides being normalizable, Ψ must be single-valued, since P can have only one value at a particular place and time, and continuous. Momentum considerations (see the Appendix to this chapter) require that the partial derivatives $\partial\Psi/\partial x$, $\partial\Psi/\partial y$, $\partial\Psi/\partial z$ be finite, continuous, and single-valued. Only wave functions with all these properties can yield physically meaningful results when used in calculations, so only such “well-behaved” wave functions are admissible as mathematical representations of real bodies. To summarize:

1. Ψ must be continuous and single-valued everywhere.
2. $\partial\Psi/\partial x$, $\partial\Psi/\partial y$, $\partial\Psi/\partial z$ must be continuous and single-valued everywhere.
3. Ψ must be normalizable, which means that Ψ must go to 0 as $x \rightarrow \pm\infty$, $y \rightarrow \pm\infty$, $z \rightarrow \pm\infty$ in order that $\int |\Psi|^2 dV$ over all space be a finite constant.

The above rules are not always obeyed by the wave functions of particles in model situations that only approximate actual ones. For instance, the wave functions of a particle in a box with infinitely hard walls do not have continuous derivatives at the walls, since $\Psi = 0$ outside the box (see Fig. 5.4). But in the real world, where walls are never infinitely hard, there is no sharp change in Ψ at the walls (see Fig. 5.7) and the derivatives are continuous. Exercise 7 gives another example of a wave function that is not well-behaved.

Partial Derivatives

Suppose we have a function $f(x, y)$ of two variables, x and y , and we want to know how f varies with only one of them, say x . To find out, we differentiate f with respect to x while treating the other variable y as a constant. The result is the **partial derivative** of f with respect to x , which is written $\partial f / \partial x$:

$$\frac{\partial f}{\partial x} = \left(\frac{df}{dx} \right)_{y=\text{constant}}$$

The rules for ordinary differentiation hold for partial differentiation as well. For instance, if $f = cx^2$,

$$\frac{df}{dx} = 2cx$$

and so, if $f = yx^2$,

$$\frac{\partial f}{\partial x} = \left(\frac{df}{dx} \right)_{y=\text{constant}} = 2yx$$

The partial derivative of $f = yx^2$ with respect to the other variable, y , is

$$\frac{\partial f}{\partial y} = \left(\frac{df}{dy} \right)_{x=\text{constant}} = x^2$$

Second order partial derivatives occur often in physics, as in the wave equation. To find $\partial^2 f / \partial x^2$, we first calculate $\partial f / \partial x$ and then differentiate again, still keeping y constant:

$\frac{\partial^2 f}{\partial x^2} = \frac{\partial}{\partial x} \left(\frac{\partial f}{\partial x} \right)$. For $f = yx^2$, $\frac{\partial^2 f}{\partial x^2} = \frac{\partial}{\partial x} (2yx) = 2y$. Similarly $\frac{\partial^2 f}{\partial x^2} = \frac{\partial}{\partial y} (x^2) = 0$

Given a normalized and otherwise acceptable wave function Ψ , the probability that the particle it describes will be found in a certain region is simply the integral of the probability density $|\Psi|^2$ over that region. Thus for a particle restricted to motion in the x direction, the probability of finding it between x_1 and x_2 is given by

Probability

$$P_{x_1 x_2} = \int_{x_1}^{x_2} |\Psi|^2 dx \quad (5.2)$$

We will see examples of such calculations later in this chapter and in the next chapter.

5.2 THE WAVE EQUATION

It can have a variety of solutions, including complex ones

Schrödinger's equation, which is the fundamental equation of quantum mechanics in the same sense that the second law of motion is the fundamental equation of newtonian mechanics, is a wave equation in the variable Ψ .

Before we tackle Schrödinger's equation, let us review the wave equation

Wave equation

$$\frac{\partial^2 y}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 y}{\partial t^2} \quad (5.3)$$

which governs a wave whose variable quantity is y that propagates in the x direction with the speed v . In the case of a wave in a stretched string, y is the displacement of the string from the x axis; in the case of a sound wave, y is the pressure difference; in the case of a light wave, y is either the electric or the magnetic field magnitude. Equation (5.3) can be derived from the second law of motion for mechanical waves and from Maxwell's equations for electromagnetic waves.

Solutions of the wave equation may be of many kinds, reflecting the variety of waves that can occur—a single traveling pulse, a train of waves of constant amplitude and wavelength, a train of superposed waves of the same amplitudes and wavelengths, a train of superposed waves of different amplitudes and wavelengths, a standing wave in a string fastened at both ends, and so on. All solutions must be of the form

$$y = F\left(t \pm \frac{x}{v}\right) \quad (5.4)$$

where F is any function that can be differentiated. The solutions $F(t - x/v)$ represent waves traveling in the $+x$ direction, and the solutions $F(t + x/v)$ represent waves traveling in the $-x$ direction.

Let us consider the wave equivalent of a “free particle,” which is a particle that is not under the influence of any forces and therefore pursues a straight path at constant speed. This wave is described by the general solution of Eq. (5.3) for undamped (that is, constant amplitude A), monochromatic (constant angular frequency ω) harmonic waves in the $+x$ direction, namely

$$y = Ae^{-i\omega(t-x/v)} \quad (5.5)$$

In this formula y is a complex quantity, with both real and imaginary parts.

Because $e^{-i\theta} = \cos \theta - i \sin \theta$, Eq. (5.5) can be written in the form

$$y = A \cos \omega \left(t - \frac{x}{v} \right) - iA \sin \omega \left(t - \frac{x}{v} \right) \quad (5.6)$$

Only the real part of Eq. (5.6) [which is the same as Eq. (3.5)] has significance in the case of waves in a stretched string. There y represents the displacement of the string from its normal position (Fig. 5.1), and the imaginary part of Eq. (5.6) is discarded as irrelevant.

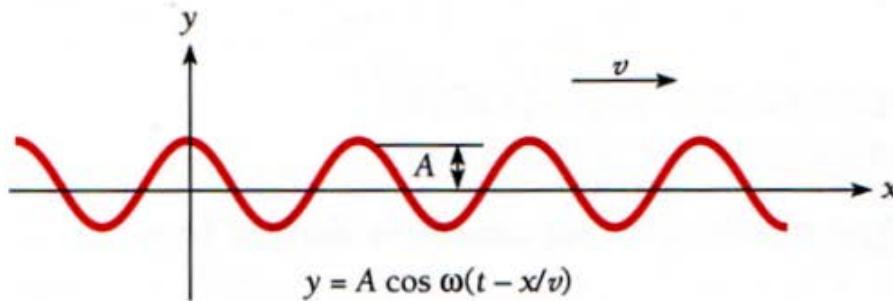


Figure 5.1 Waves in the xy plane traveling in the $+x$ direction along a stretched string lying on the x axis.

5.3 SCHRÖDINGER'S EQUATION: TIME-DEPENDENT FORM

A basic physical principle that cannot be derived from anything else

In quantum mechanics the wave function Ψ corresponds to the wave variable y of wave motion in general. However, Ψ , unlike y , is not itself a measurable quantity and may therefore be complex. For this reason we assume that Ψ for a particle moving freely in the $+x$ direction is specified by

$$\Psi = Ae^{-i\omega(t-x/v)} \quad (5.7)$$

Replacing ω in the above formula by $2\pi\nu$ and v by $\lambda\nu$ gives

$$\Psi = Ae^{-2\pi i(\nu t - x/\lambda)} \quad (5.8)$$

This is convenient since we already know what ν and λ are in terms of the total energy E and momentum p of the particle being described by Ψ . Because

$$E = h\nu = 2\pi\hbar\nu \quad \text{and} \quad \lambda = \frac{h}{p} = \frac{2\pi\hbar}{p}$$

we have

Free particle

$$\Psi = Ae^{-(i/\hbar)(Et - px)} \quad (5.9)$$

Free particle

$$\Psi = Ae^{-(i/\hbar)(Et - px)} \quad (5.9)$$

Equation (5.9) describes the wave equivalent of an unrestricted particle of total energy E and momentum p moving in the $+x$ direction, just as Eq. (5.5) describes, for example, a harmonic displacement wave moving freely along a stretched string.

The expression for the wave function Ψ given by Eq. (5.9) is correct only for freely moving particles. However, we are most interested in situations where the motion of a particle is subject to various restrictions. An important concern, for example, is an electron bound to an atom by the electric field of its nucleus. What we must now do is obtain the fundamental differential equation for Ψ , which we can then solve for Ψ in a specific situation. This equation, which is Schrödinger's equation, can be arrived at in various ways, but it *cannot* be rigorously derived from existing physical principles: the equation represents something new. What will be done here is to show one route to the wave equation for Ψ and then to discuss the significance of the result.

Free particle

$$\Psi = Ae^{-(i/\hbar)(Et - px)} \quad (5.9)$$

We begin by differentiating Eq. (5.9) for Ψ twice with respect to x , which gives

$$\frac{\partial^2 \Psi}{\partial x^2} = -\frac{p^2}{\hbar^2} \Psi$$

$p^2 \Psi = -\hbar^2 \frac{\partial^2 \Psi}{\partial x^2}$

(5.10)

Differentiating Eq. (5.9) once with respect to t gives

$$\frac{\partial \Psi}{\partial t} = -\frac{iE}{\hbar} \Psi$$

$E \Psi = -\frac{\hbar}{i} \frac{\partial \Psi}{\partial t}$

(5.11)

At speeds small compared with that of light, the total energy E of a particle is the sum of its kinetic energy $p^2/2m$ and its potential energy U , where U is in general a function of position x and time t :

$$E = \frac{p^2}{2m} + U(x, t) \quad (5.12)$$

$$E = \frac{p^2}{2m} + U(x, t) \quad (5.12)$$

The function U represents the influence of the rest of the universe on the particle. Of course, only a small part of the universe interacts with the particle to any extent; for instance, in the case of the electron in a hydrogen atom, only the electric field of the nucleus must be taken into account.

Multiplying both sides of Eq. (5.12) by the wave function Ψ gives

$$E\Psi = \frac{p^2\Psi}{2m} + U\Psi \quad (5.13)$$

Now we substitute for $E\Psi$ and $p^2\Psi$ from Eqs. (5.10) and (5.11) to obtain the **time-dependent form of Schrödinger's equation**:

**Time-dependent
Schrödinger
equation in one
dimension**

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + U\Psi \quad (5.14)$$

Time-dependent Schrödinger equation in one dimension

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + U\Psi \quad (5.14)$$

In three dimensions the time-dependent form of Schrödinger's equation is

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} \right) + U\Psi \quad (5.15)$$

where the particle's potential energy U is some function of x , y , z , and t .

Any restrictions that may be present on the particle's motion will affect the potential-energy function U . Once U is known, Schrödinger's equation may be solved for the wave function Ψ of the particle, from which its probability density $|\Psi|^2$ may be determined for a specified x , y , z , t .

Schrödinger's equation was obtained here using the wave function of a freely moving particle (potential energy $U = \text{constant}$). How can we be sure it applies to the general case of a particle subject to arbitrary forces that vary in space and time [$U = U(x, y, z, t)$]? Substituting Eqs. (5.10) and (5.11) into Eq. (5.13) is really a wild leap with no formal justification; this is true for all other ways in which Schrödinger's equation can be arrived at, including Schrödinger's own approach.

What we must do is postulate Schrödinger's equation, solve it for a variety of physical situations, and compare the results of the calculations with the results of experiments. If both sets of results agree, the postulate embodied in Schrödinger's equation is valid. If they disagree, the postulate must be discarded and some other approach would then have to be explored. In other words,

Schrödinger's equation cannot be derived from other basic principles of physics; it is a basic principle in itself.

What has happened is that Schrödinger's equation has turned out to be remarkably accurate in predicting the results of experiments. To be sure, Eq. (5.15) can be used only for nonrelativistic problems, and a more elaborate formulation is needed when particle speeds near that of light are involved. But because it is in accord with experience within its range of applicability, we must consider Schrödinger's equation as a valid statement concerning certain aspects of the physical world.

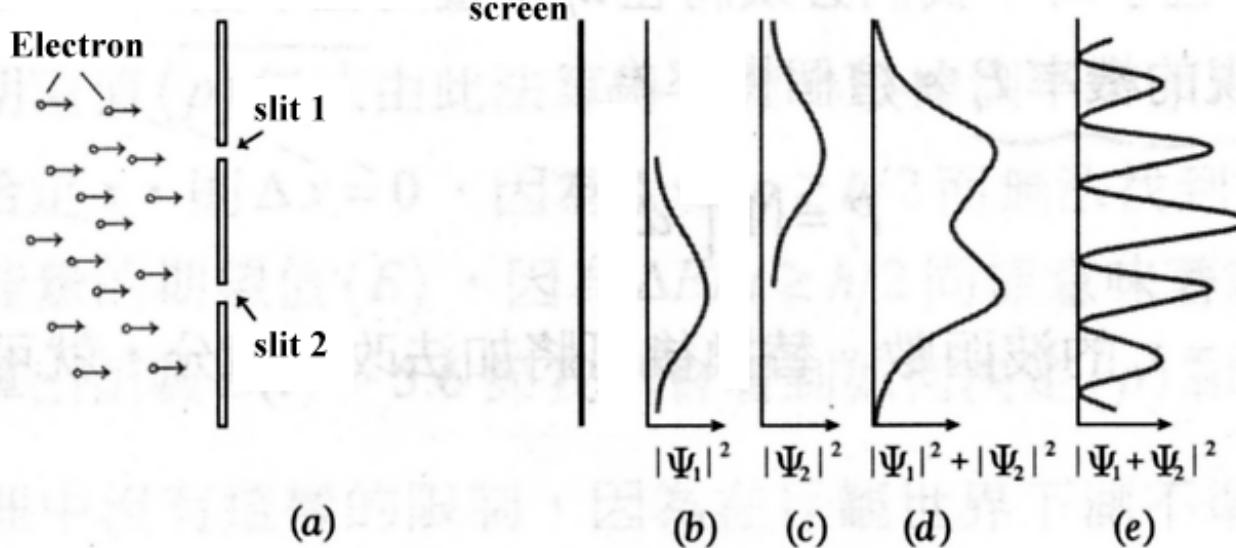
It is worth noting that Schrödinger's equation does not increase the number of principles needed to describe the workings of the physical world. Newton's second law of motion $F = ma$, the basic principle of classical mechanics, can be derived from Schrödinger's equation provided the quantities it relates are understood to be averages rather than precise values.

Linearity and Superposition

An important property of Schrödinger's equation is that it is linear in the wave function Ψ . By this is meant that the equation has terms that contain Ψ and its derivatives but no terms independent of Ψ or that involve higher powers of Ψ or its derivatives. As a result, a linear combination of solutions of Schrödinger's equation for a given system is also itself a solution. If Ψ_1 and Ψ_2 are two solutions (that is, two wave functions that satisfy the equation), then

$$\Psi = a_1\Psi_1 + a_2\Psi_2$$

is also a solution, where a_1 and a_2 are constants (see Exercise 8). Thus the wavefunctions Ψ_1 and Ψ_2 obey the superposition principle that other waves do (see Sec. 2.1) and we conclude that interference effects can occur for wave functions just as they can for light, sound, water, and electromagnetic waves. In fact, the discussions of Secs. 3.4 and 3.7 assumed that de Broglie waves are subject to the superposition principle.



(a) Double slits experiment, (b) only slit 1 open, (c) only slit 2 open
 (d) sum of (b) and (c), (e) both slits 1 and 2 open

$$(b) P_1 = |\Psi_1|^2 = \Psi_1^* \Psi_1 \quad (c) P_2 = |\Psi_2|^2 = \Psi_2^* \Psi_2 \quad (d) |\Psi_1|^2 + |\Psi_2|^2$$

$$(e) \Psi = \Psi_1 + \Psi_2$$

$$P = |\Psi|^2 = |\Psi_1 + \Psi_2|^2 = (\Psi_1^* + \Psi_2^*)(\Psi_1 + \Psi_2)$$

$$= \Psi_1^* \Psi_1 + \Psi_2^* \Psi_2 + \Psi_1^* \Psi_2 + \Psi_2^* \Psi_1$$

$$= P_1 + P_2 + \underline{\Psi_1^* \Psi_2 + \Psi_2^* \Psi_1}$$

5.4 EXPECTATION VALUES

How to extract information from a wave function

Once Schrödinger's equation has been solved for a particle in a given physical situation, the resulting wave function $\Psi(x, y, z, t)$ contains all the information about the particle that is permitted by the uncertainty principle. Except for those variables that are quantized this information is in the form of probabilities and not specific numbers.

As an example, let us calculate the expectation value $\langle x \rangle$ of the position of a particle confined to the x axis that is described by the wave function $\Psi(x, t)$. This is the value of x we would obtain if we measured the positions of a great many particles described by the same wave function at some instant t and then averaged the results.

To make the procedure clear, we first answer a slightly different question: What is the average position \bar{x} of a number of identical particles distributed along the x axis in such a way that there are N_1 particles at x_1 , N_2 particles at x_2 , and so on? The average position in this case is the same as the center of mass of the distribution, and so

$$\bar{x} = \frac{N_1x_1 + N_2x_2 + N_3x_3 + \dots}{N_1 + N_2 + N_3 + \dots} = \frac{\sum N_i x_i}{\sum N_i} \quad (5.16)$$

When we are dealing with a single particle, we must replace the number N_i of particles at x_i by the probability P_i that the particle be found in an interval dx at x_i . This probability is

$$P_i = |\Psi_i|^2 dx \quad (5.17)$$

where Ψ_i is the particle wave function evaluated at $x = x_i$. Making this substitution and changing the summations to integrals, we see that the expectation value of the position of the single particle is

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} x |\Psi|^2 dx}{\int_{-\infty}^{\infty} |\Psi|^2 dx} \quad (5.18)$$

If Ψ is a normalized wave function, the denominator of Eq. (5.18) equals the probability that the particle exists somewhere between $x = -\infty$ and $x = \infty$ and therefore has the value 1. In this case

**Expectation value
for position**

$$\langle x \rangle = \int_{-\infty}^{\infty} x |\Psi|^2 dx \quad (5.19)$$

This formula states that $\langle x \rangle$ is located at the center of mass (so to speak) of $|\Psi|^2$. If $|\Psi|^2$ is plotted versus x on a graph and the area enclosed by the curve and the x axis is cut out, the balance point will be at $\langle x \rangle$.

Example 5.2

A particle limited to the x axis has the wave function $\Psi = ax$ between $x = 0$ and $x = 1$; $\Psi = 0$ elsewhere. (a) Find the probability that the particle can be found between $x = 0.45$ and $x = 0.55$. (b) Find the expectation value $\langle x \rangle$ of the particle's position.

Solution

(a) The probability is

$$\int_{x_1}^{x_2} |\Psi|^2 dx = a^2 \int_{0.45}^{0.55} x^2 dx = a^2 \left[\frac{x^3}{3} \right]_{0.45}^{0.55} = 0.0251a^2$$

(b) The expectation value is

$$\langle x \rangle = \int_0^1 x|\Psi|^2 dx = a^2 \int_0^1 x^3 dx = a^2 \left[\frac{x^4}{4} \right]_0^1 = \frac{a^2}{4}$$

The same procedure as that followed above can be used to obtain the expectation value $\langle G(x) \rangle$ of any quantity—for instance, potential energy $U(x)$ —that is a function of the position x of a particle described by a wave function Ψ . The result is

Expectation value

$$\langle G(x) \rangle = \int_{-\infty}^{\infty} G(x) |\Psi|^2 dx \quad (5.20)$$

The expectation value $\langle p \rangle$ for momentum cannot be calculated this way because, according to the uncertainty principles, no such function as $p(x)$ can exist. If we specify x , so that $\Delta x = 0$, we cannot specify a corresponding p since $\Delta x \Delta p \geq \hbar/2$. The same problem occurs for the expectation value $\langle E \rangle$ for energy. The Appendix to this chapter discusses how $\langle p \rangle$ and $\langle E \rangle$ can be found without violating the uncertainty principle.

Link to p. 71

5.5 SCHRÖDINGER'S EQUATION: STEADY-STATE FORM

Eigenvalues and eigenfunctions

In a great many situations the potential energy of a particle does not depend on time explicitly; the forces that act on it, and hence U , vary with the position of the particle only. When this is true, Schrödinger's equation may be simplified by removing all reference to t .

We begin by noting that the one-dimensional wave function Ψ of an unrestricted particle may be written

$$\Psi = Ae^{-(i/\hbar)(Et - px)} = Ae^{-(iE/\hbar)t}e^{+(ip/\hbar)x} = \psi e^{-(iE/\hbar)t} \quad (5.21)$$

Evidently Ψ is the product of a time-dependent function $e^{-(iE/\hbar)t}$ and a position-dependent function ψ . As it happens, the time variations of *all* wave functions of particles acted on by stationary forces have the same form as that of an unrestricted particle.

An important property of Schrödinger's steady-state equation is that, if it has one or more solutions for a given system, each of these wave functions corresponds to a specific value of the energy E . Thus energy quantization appears in wave mechanics as a natural element of the theory, and energy quantization in the physical world is revealed as a universal phenomenon characteristic of *all* stable systems.

Substituting the Ψ of Eq. (5.21) into the time-dependent form of Schrödinger's equation, we find that

$$E\psi e^{-(iE/\hbar)t} = -\frac{\hbar^2}{2m}e^{-(iE/\hbar)t}\frac{\partial^2\psi}{\partial x^2} + U\psi e^{-(iE/\hbar)t}$$

Dividing through by the common exponential factor gives

**Steady-state
Schrödinger
equation in one
dimension**

$$\frac{\partial^2\psi}{\partial x^2} + \frac{2m}{\hbar^2}(E - U)\psi = 0 \quad (5.22)$$

Equation (5.22) is the **steady-state form of Schrödinger's equation**. In three dimensions it is

**Steady-state
Schrödinger
equation in three
dimensions**

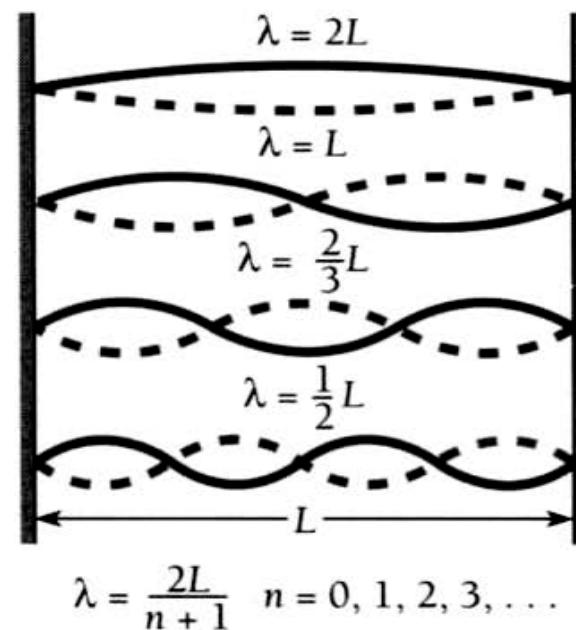
$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{2m}{\hbar^2}(E - U)\psi = 0 \quad (5.23)$$

A familiar and quite close analogy to the manner in which energy quantization occurs in solutions of Schrödinger's equation is with standing waves in a stretched string of length L that is fixed at both ends. Here, instead of a single wave propagating indefinitely in one direction, waves are traveling in both the $+x$ and $-x$ directions simultaneously. These waves are subject to the condition (called a **boundary condition**) that the displacement y always be zero at both ends of the string. An acceptable function $y(x, t)$ for the displacement must, with its derivatives (except at the ends), be as well-behaved as ψ and its derivatives—that is, be continuous, finite, and single-valued. In this case y must be real, not complex, as it represents a directly measurable quantity. The only solutions of the wave equation, Eq. (5.3), that are in accord with these various limitations are those in which the wavelengths are given by

$$\lambda_n = \frac{2L}{n + 1} \quad n = 0, 1, 2, 3, \dots$$

as shown in Fig. 5.2. It is the *combination* of the wave equation and the restrictions placed on the nature of its solution that leads us to conclude that $y(x, t)$ can exist only for certain wavelengths λ_n .

Figure 5.2 Standing waves in a stretched string fastened at both ends.



$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2}(E - U)\psi = 0$$

Eigenvalues and Eigenfunctions

The values of energy E_n for which Schrödinger's steady-state equation can be solved are called **eigenvalues** and the corresponding wave functions ψ_n are called **eigenfunctions**. (These terms come from the German *Eigenwert*, meaning “proper or characteristic value,” and *Eigenfunktion*, “proper or characteristic function.”) The discrete energy levels of the hydrogen atom

$$E_n = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2}\left(\frac{1}{n^2}\right) \quad n = 1, 2, 3, \dots$$

are an example of a set of eigenvalues. We shall see in Chap. 6 why these particular values of E are the only ones that yield acceptable wave functions for the electron in the hydrogen atom.

An important example of a dynamical variable other than total energy that is found to be quantized in stable systems is angular momentum \mathbf{L} . In the case of the hydrogen atom, we shall find that the eigenvalues of the magnitude of the total angular momentum are specified by

$$L = \sqrt{l(l+1)}\hbar \quad l = 0, 1, 2, \dots, (n-1)$$

Of course, a dynamical variable G may not be quantized. In this case measurements of G made on a number of identical systems will not yield a unique result but instead a spread of values whose average is the expectation value

$$\langle G \rangle = \int_{-\infty}^{\infty} G|\psi|^2 dx$$

In the hydrogen atom, the electron's position is not quantized, for instance, so that we must think of the electron as being present in the vicinity of the nucleus with a certain probability $|\psi|^2$ per unit volume but with no predictable position or even orbit in the classical sense. This probabilistic statement does not conflict with the fact that experiments performed on hydrogen atoms always show that each one contains a whole electron, not 27 percent of an electron in a certain region and 73 percent elsewhere. The probability is one of *finding* the electron, and although this probability is smeared out in space, the electron itself is not.

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2}(E - U)\psi = 0$$

5.6 PARTICLE IN A BOX

How boundary conditions and normalization determine wave functions

To solve Schrödinger's equation, even in its simpler steady-state form, usually requires elaborate mathematical techniques. For this reason the study of quantum mechanics has traditionally been reserved for advanced students who have the required proficiency in mathematics. However, since quantum mechanics is the theoretical structure whose results are closest to experimental reality, we must explore its methods and applications to understand modern physics. As we shall see, even a modest mathematical background is enough for us to follow the trains of thought that have led quantum mechanics to its greatest achievements.

The simplest quantum-mechanical problem is that of a particle trapped in a box with infinitely hard walls. In Sec. 3.6 we saw how a quite simple argument yields the energy levels of the system. Let us now tackle the same problem in a more formal way, which will give us the wave function ψ_n that corresponds to each energy level.

We may specify the particle's motion by saying that it is restricted to traveling along the x axis between $x = 0$ and $x = L$ by infinitely hard walls. A particle does not lose energy when it collides with such walls, so that its total energy stays constant. From a formal point of view the potential energy U of the particle is infinite on both sides of the box, while U is a constant—say 0 for convenience—on the inside (Fig. 5.3). Because the particle cannot have an infinite amount of energy, it cannot exist outside the box, and so its wave function ψ is 0 for $x \leq 0$ and $x \geq L$. Our task is to find what ψ is within the box, namely, between $x = 0$ and $x = L$.

Within the box Schrödinger's equation becomes

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} E \psi = 0 \quad (5.24)$$

since $U = 0$ there. (The total derivative $d^2\psi/dx^2$ is the same as the partial derivative $\partial^2\psi/\partial x^2$ because ψ is a function only of x in this problem.)

Equation (5.24) has the solution

$$\psi = A \sin \frac{\sqrt{2mE}}{\hbar} x + B \cos \frac{\sqrt{2mE}}{\hbar} x \quad (5.25)$$

which we can verify by substitution back into Eq. (5.24). A and B are constants to be evaluated.

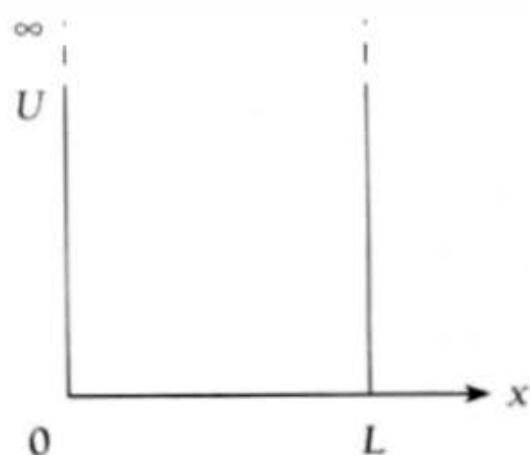


Figure 5.3 A square potential well with infinitely high barriers at each end corresponds to a box with infinitely hard walls.

This solution is subject to the boundary conditions that $\psi = 0$ for $x = 0$ and for $x = L$. Since $\cos 0 = 1$, the second term cannot describe the particle because it does not vanish at $x = 0$. Hence we conclude that $B = 0$. Since $\sin 0 = 0$, the sine term always yields $\psi = 0$ at $x = 0$, as required, but ψ will be 0 at $x = L$ only when

$$\frac{\sqrt{2mE}}{\hbar} L = n\pi \quad n = 1, 2, 3, \dots \quad (5.26)$$

This result comes about because the sines of the angles $\pi, 2\pi, 3\pi, \dots$ are all 0.

From Eq. (5.26) it is clear that the energy of the particle can have only certain values, which are the eigenvalues mentioned in the previous section. These eigenvalues, constituting the **energy levels** of the system, are found by solving Eq. (5.26) for E_n , which gives

Particle in a box $E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \quad n = 1, 2, 3, \dots \quad (5.27)$

Equation (5.27) is the same as Eq. (3.18) and has the same interpretation [see the discussion that follows Eq. (3.18) in Sec. 3.6].

Wave Functions of a Particle in a Box

The wave functions of a particle in a box whose energies are E_n are, from Eq. (5.25) with $B = 0$,

$$\psi_n = A \sin \frac{\sqrt{2mE_n}}{\hbar} x \quad (5.28)$$

Substituting Eq. (5.27) for E_n gives

$$\psi_n = A \sin \frac{n\pi x}{L} \quad (5.29)$$

for the eigenfunctions corresponding to the energy eigenvalues E_n .

It is easy to verify that these eigenfunctions meet all the requirements discussed in Sec. 5.1: for each quantum number n , ψ_n is a finite, single-valued function of x , and ψ_n and $\partial\psi_n/\partial x$ are continuous (except at the ends of the box). Furthermore, the integral of $|\psi_n|^2$ over all space is finite, as we can see by integrating $|\psi_n|^2 dx$ from $x = 0$ to $x = L$ (since the particle is confined within these limits). With the help of the trigonometric identity $\sin^2 \theta = \frac{1}{2}(1 - \cos 2\theta)$ we find that

$$\begin{aligned}
 \int_{-\infty}^{\infty} |\psi_n|^2 dx &= \int_0^L |\psi_n|^2 dx = A^2 \int_0^L \sin^2 \left(\frac{n\pi x}{L} \right) dx \\
 &= \frac{A^2}{2} \left[\int_0^L dx - \int_0^L \cos \left(\frac{2n\pi x}{L} \right) dx \right] \\
 &= \frac{A^2}{2} \left[x - \left(\frac{L}{2n\pi} \right) \sin \frac{2n\pi x}{L} \right]_0^L = A^2 \left(\frac{L}{2} \right)
 \end{aligned} \tag{5.30}$$

To normalize ψ we must assign a value to A such that $|\psi_n|^2 dx$ is *equal* to the probability $P dx$ of finding the particle between x and $x + dx$, rather than merely proportional to $P dx$. If $|\psi_n|^2 dx$ is to equal $P dx$, then it must be true that

$$\int_{-\infty}^{\infty} |\psi_n|^2 dx = 1 \quad (5.31)$$

Comparing Eqs. (5.30) and (5.31), we see that the wave functions of a particle in a box are normalized if

$$A = \sqrt{\frac{2}{L}} \quad (5.32)$$

The normalized wave functions of the particle are therefore

Particle in a box $\psi_n = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \quad n = 1, 2, 3, \dots \quad (5.33)$

Particle in a box $\psi_n = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \quad n = 1, 2, 3, \dots \quad (5.33)$

The normalized wave functions ψ_1 , ψ_2 , and ψ_3 together with the probability densities $|\psi_1|^2$, $|\psi_2|^2$, and $|\psi_3|^2$ are plotted in Fig. 5.4. Although ψ_n may be negative as well as positive, $|\psi_n|^2$ is always positive and, since ψ_n is normalized, its value at a given x is equal to the probability density of finding the particle there. In every case $|\psi_n|^2 = 0$ at $x = 0$ and $x = L$, the boundaries of the box.

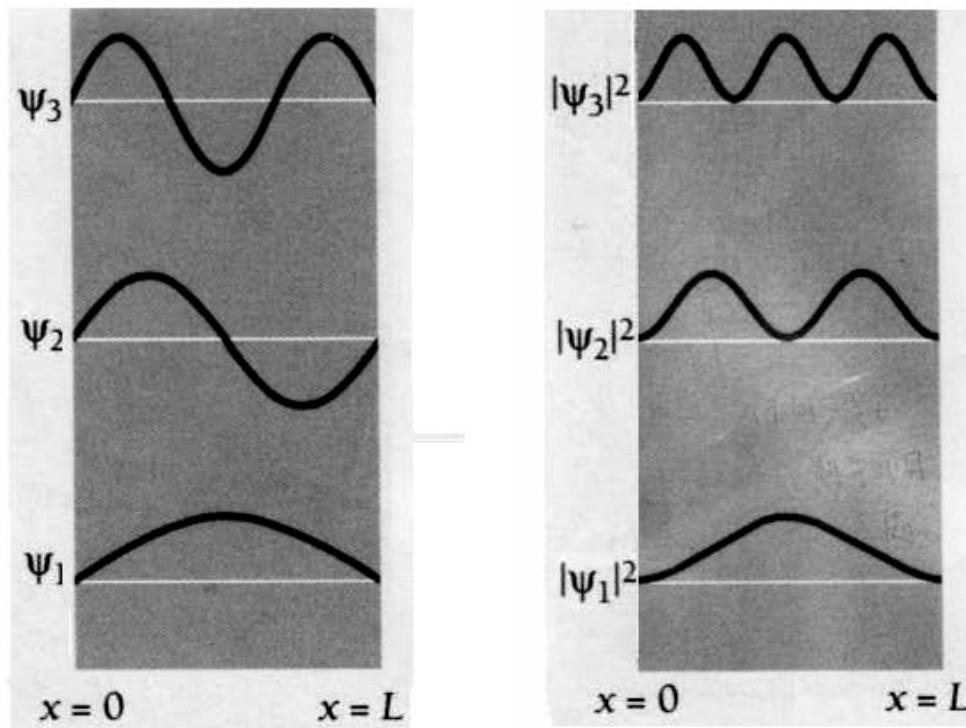


Figure 5.4 Wave functions and probability densities of a particle confined to a box with rigid walls.

At a particular place in the box the probability of the particle being present may be very different for different quantum numbers. For instance, $|\psi_1|^2$ has its maximum value of $2/L$ in the middle of the box, while $|\psi_2|^2 = 0$ there. A particle in the lowest energy level of $n = 1$ is most likely to be in the middle of the box, while a particle in the next higher state of $n = 2$ is *never* there! Classical physics, of course, suggests the same probability for the particle being anywhere in the box.

The wave functions shown in Fig. 5.4 resemble the possible vibrations of a string fixed at both ends, such as those of the stretched string of Fig. 5.2. This follows from the fact that waves in a stretched string and the wave representing a moving particle are described by equations of the same form, so that when identical restrictions are placed upon each kind of wave, the formal results are identical.

Example 5.3

Find the probability that a particle trapped in a box L wide can be found between $0.45L$ and $0.55L$ for the ground and first excited states.

Solution

This part of the box is one-tenth of the box's width and is centered on the middle of the box (Fig. 5.5). Classically we would expect the particle to be in this region 10 percent of the time. Quantum mechanics gives quite different predictions that depend on the quantum number of the particle's state. From Eqs. (5.2) and (5.33) the probability of finding the particle between x_1 and x_2 when it is in the n th state is

$$\begin{aligned} P_{x_1 x_2} &= \int_{x_1}^{x_2} |\psi_n|^2 dx = \frac{2}{L} \int_{x_1}^{x_2} \sin^2 \frac{n\pi x}{L} dx \\ &= \left[\frac{x}{L} - \frac{1}{2n\pi} \sin \frac{2n\pi x}{L} \right]_{x_1}^{x_2} \end{aligned}$$

Here $x_1 = 0.45L$ and $x_2 = 0.55L$. For the ground state, which corresponds to $n = 1$, we have

$$P_{x_1 x_2} = 0.198 = 19.8 \text{ percent}$$

This is about twice the classical probability. For the first excited state, which corresponds to $n = 2$, we have $P_{x_1 x_2} = 0.0065 = 0.65 \text{ percent}$

This low figure is consistent with the probability density of $|\psi_n|^2 = 0$ at $x = 0.5L$.

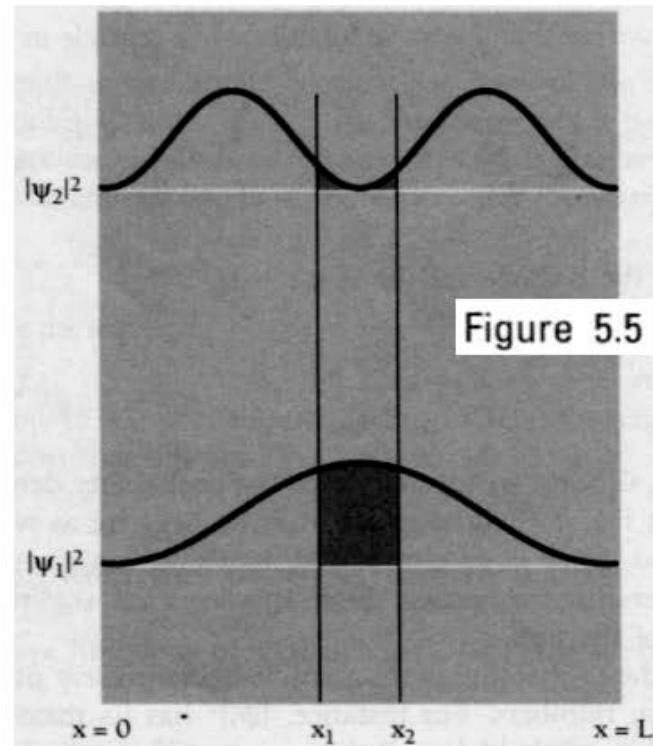


Figure 5.5

Example 5.4

Find the expectation value $\langle x \rangle$ of the position of a particle trapped in a box L wide.

Solution

From Eqs. (5.19) and (5.33) we have

$$\begin{aligned}\langle x \rangle &= \int_{-\infty}^{\infty} x |\psi|^2 dx = \frac{2}{L} \int_0^L x \sin^2 \frac{n\pi x}{L} dx \\ &= \frac{2}{L} \left[\frac{x^2}{4} - \frac{x \sin(2n\pi x/L)}{4n\pi/L} - \frac{\cos(2n\pi x/L)}{8(n\pi/L)^2} \right]_0^L\end{aligned}$$

Since $\sin n\pi = 0$, $\cos 2n\pi = 1$, and $\cos 0 = 1$, for all the values of n the expectation value of x is

$$\langle x \rangle = \frac{2}{L} \left(\frac{L^2}{4} \right) = \frac{L}{2}$$

This result means that the average position of the particle is the middle of the box in all quantum states. There is no conflict with the fact that $|\psi|^2 = 0$ at $L/2$ in the $n = 2, 4, 6, \dots$ states because $\langle x \rangle$ is an *average*, not a probability, and it reflects the symmetry of $|\psi|^2$ about the middle of the box. (See the Appendix to this chapter for a calculation of the expectation value $\langle p \rangle$ of the particle's momentum.)

5.7 FINITE POTENTIAL WELL

The wave function penetrates the walls, which lowers the energy levels

Potential energies are never infinite in the real world, and the box with infinitely hard walls of the previous section has no physical counterpart. However, potential wells with barriers of finite height certainly do exist. Let us see what the wave functions and energy levels of a particle in such a well are.

Figure 5.6 shows a potential well with square corners that is U high and L wide and contains a particle whose energy E is less than U . According to classical mechanics, when the particle strikes the sides of the well, it bounces off without entering regions I and III. In quantum mechanics, the particle also bounces back and forth, but now it has a certain probability of penetrating into regions I and III even though $E < U$. In regions I and III Schrödinger's steady-state equation is

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

which we can rewrite in the more convenient form

$$\frac{d^2\psi}{dx^2} - a^2\psi = 0 \quad \begin{cases} x < 0 \\ x > L \end{cases} \quad (5.34)$$

$$\text{where } a = \frac{\sqrt{2m(U - E)}}{\hbar} \quad (5.35)$$

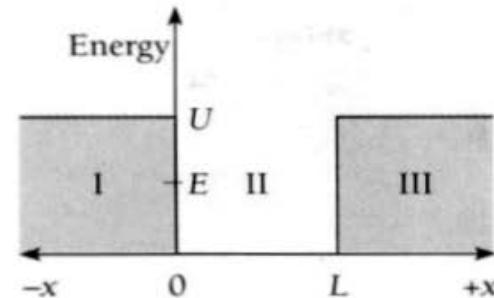


Figure 5.6 A square potential well with finite barriers. The energy E of the trapped particle is less than the height U of the barriers.

$$\frac{d^2\psi}{dx^2} - a^2\psi = 0 \quad \begin{cases} x < 0 \\ x > L \end{cases} \quad (5.34)$$

The solutions to Eq. (5.34) are real exponentials:

$$\psi_I = Ae^{ax} + Be^{-ax} \quad (5.36)$$

$$\psi_{III} = Ce^{ax} + De^{-ax} \quad (5.37)$$

Both ψ_I and ψ_{III} must be finite everywhere. Since $e^{-ax} \rightarrow \infty$ as $x \rightarrow -\infty$ and $e^{ax} \rightarrow \infty$ as $x \rightarrow \infty$, the coefficients B and C must therefore be 0. Hence we have

$$\psi_I = Ae^{ax} \quad (5.38)$$

$$\psi_{III} = De^{-ax} \quad (5.39)$$

These wave functions decrease exponentially inside the barriers at the sides of the well.

Within the well Schrödinger's equation is the same as Eq. (5.24) and its solution is again

$$\psi_{II} = E \sin \frac{\sqrt{2mE}}{\hbar} x + F \cos \frac{\sqrt{2mE}}{\hbar} x \quad (5.40)$$

In the case of a well with infinitely high barriers, we found that $F = 0$ in order that $\psi = 0$ at $x = 0$ and $x = L$. Here, however, $\psi_{II} = A$ at $x = 0$ and $\psi_{II} = D$ at $x = L$, so both the sine and cosine solutions of Eq. (5.40) are possible.

For either solution, both ψ and $d\psi/dx$ must be continuous at $x = 0$ and $x = L$: the wave functions inside and outside each side of the well must not only have the same value where they join but also the same slopes, so they match up perfectly. When these boundary conditions are taken into account, the result is that exact matching only occurs for certain specific values E_n of the particle energy. The complete wave functions and their probability densities are shown in Fig. 5.7.

Because the wavelengths that fit into the well are longer than for an infinite well of the same width (see Fig. 5.4), the corresponding particle momenta are lower (we recall that $\lambda = h/p$). Hence the energy levels E_n are lower for each n than they are for a particle in an infinite well.

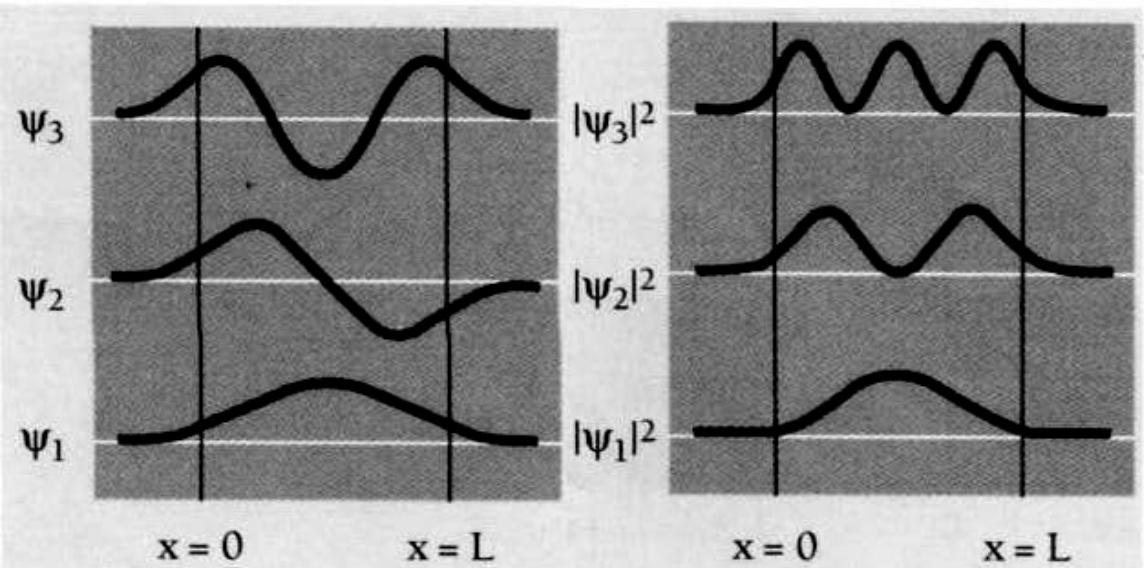


Figure 5.7 Wave functions and probability densities of a particle in a finite potential well. The particle has a certain probability of being found outside the wall.

Link to Fig.5.4

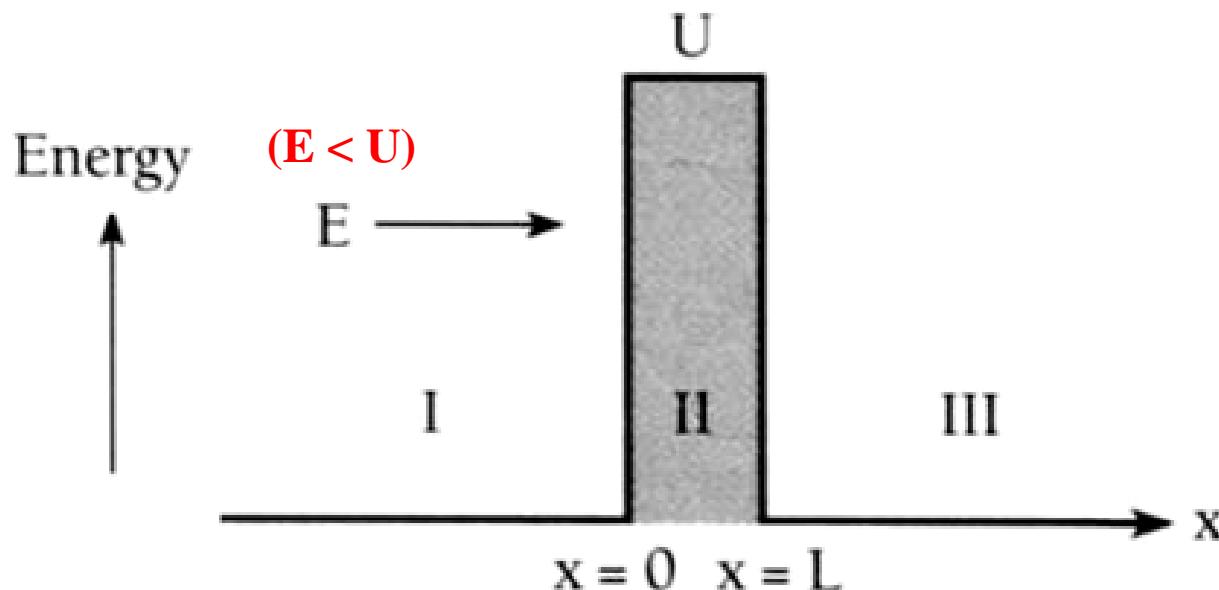
5.8 TUNNEL EFFECT

A particle without the energy to pass over a potential barrier may still tunnel through it

Although the walls of the potential well of Fig. 5.6 were of finite height, they were assumed to be infinitely thick. As a result the particle was trapped forever even though it could penetrate the walls. We next look at the situation of a particle that strikes a potential barrier of height U , again with $E < U$, but here the barrier has a finite width (Fig. 5.8). What we will find is that the particle has a certain probability—not necessarily great, but not zero either—of passing through the barrier and emerging on the other side. The particle lacks the energy to go over the top of the barrier, but it can nevertheless tunnel through it, so to speak. Not surprisingly, the higher the barrier and the wider it is, the less the chance that the particle can get through.

The **tunnel effect** actually occurs, notably in the case of the alpha particles emitted by certain radioactive nuclei. As we shall learn in Chap. 12, an alpha particle whose kinetic energy is only a few MeV is able to escape from a nucleus whose potential wall is perhaps 25 MeV high. The probability of escape is so small that the alpha particle might have to strike the wall 10^{38} or more times before it emerges, but sooner or later it does get out. Tunneling also occurs in the operation of certain semiconductor diodes (Sec. 10.7) in which electrons pass through potential barriers even though their kinetic energies are smaller than the barrier heights.

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2}(E - U)\psi = 0$$



$$U(x) = \begin{cases} 0 & x \leq 0, x \geq L \\ U & 0 < x < L \end{cases}$$

Link

Let us consider a beam of identical particles all of which have the kinetic energy E . The beam is incident from the left on a potential barrier of height U and width L , as in Fig. 5.8. On both sides of the barrier $U = 0$, which means that no forces act on the particles there. In these regions Schrödinger's equation for the particles (all of which are described by the same wave function ψ) takes the forms

$$\frac{d^2\psi_I}{dx^2} + \frac{2m}{\hbar^2} E \psi_I = 0 \quad (5.41)$$

$$\frac{d^2\psi_{III}}{dx^2} + \frac{2m}{\hbar^2} E \psi_{III} = 0 \quad (5.42)$$

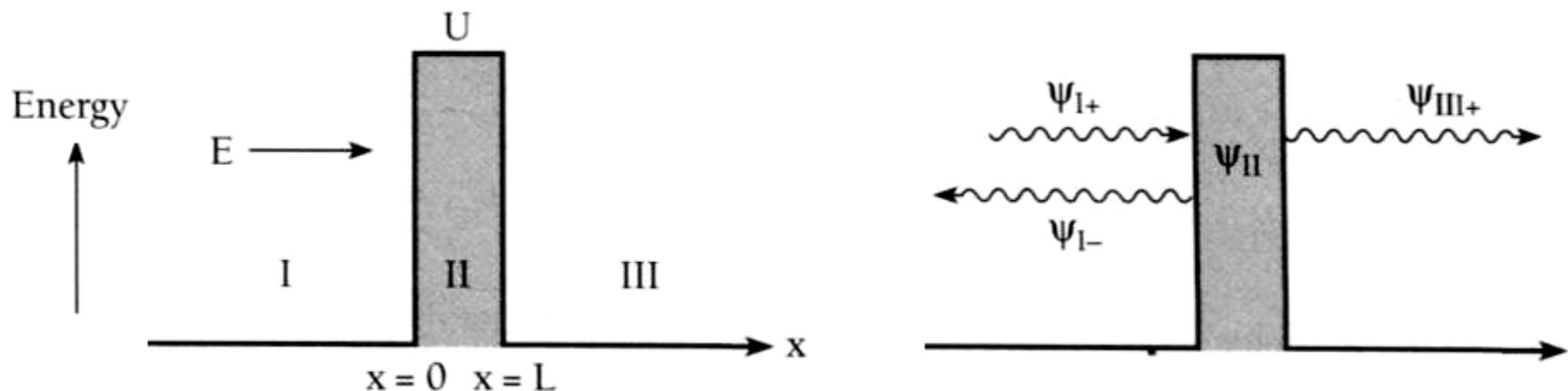
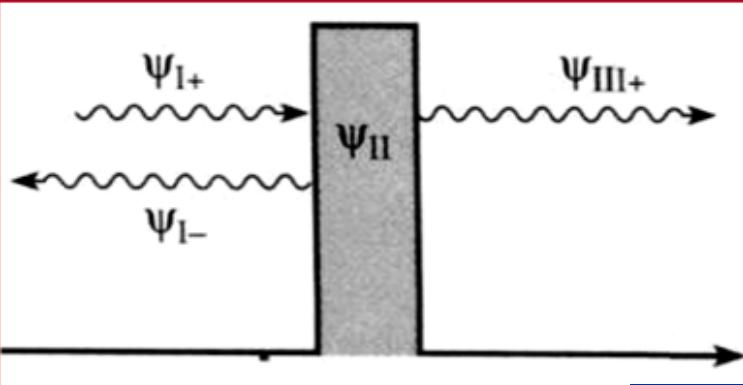


Figure 5.8 When a particle of energy $E < U$ approaches a potential barrier, according to classical mechanics the particle must be reflected. In quantum mechanics, the de Broglie waves that correspond to the particle are partly reflected and partly transmitted, which means that the particle has a finite chance of penetrating the barrier.



$$\frac{d^2\Psi_I}{dx^2} + \frac{2m}{\hbar^2} E \Psi_I = 0 \quad (5.41)$$

$$\frac{d^2\Psi_{III}}{dx^2} + \frac{2m}{\hbar^2} E \Psi_{III} = 0 \quad (5.42)$$

The solutions to these equations that are appropriate here are

$$\Psi_I = Ae^{ik_1 x} + Be^{-ik_1 x} \quad (5.43)$$

$$\Psi_{III} = Fe^{ik_1 x} + Ge^{-ik_1 x} \quad (5.44) \quad \text{where}$$

Wave number outside barrier $k_1 = \frac{\sqrt{2mE}}{\hbar} = \frac{p}{\hbar} = \frac{2\pi}{\lambda} \quad (5.45)$

is the wave number of the de Broglie waves that represent the particles outside the barrier. Because

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

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

these solutions are equivalent to Eq. (5.25)—the values of the coefficients are different in each case, of course—but are in a more suitable form to describe particles that are not trapped.

The various terms in Eqs. (5.43) and (5.44) are not hard to interpret. As shown schematically in Fig. 5.8, Ae^{ik_1x} is a wave of amplitude A incident from the left on the barrier. Hence we can write

Incoming wave

$$\psi_{1+} = Ae^{ik_1x} \quad (5.46)$$

This wave corresponds to the incident beam of particles in the sense that $|\psi_{1+}|^2$ is their probability density. If v_{1+} is the group velocity of the incoming wave, which equals the velocity of the particles, then

$$S = |\psi_{1+}|^2 v_{1+}$$

Link

is the flux of particles that arrive at the barrier. That is, S is the number of particles per square meter per second that arrive there.

At $x = 0$ the incident wave strikes the barrier and is partially reflected, with

Reflected wave

$$\psi_{1-} = Be^{-ik_1x} \quad (5.47)$$

representing the reflected wave. Hence

$$\psi_1 = \psi_{1+} + \psi_{1-} \quad (5.48)$$

On the far side of the barrier ($x > L$) there can only be a wave

Transmitted wave

$$\psi_{III+} = Fe^{ik_1x} \quad (5.49)$$

traveling in the $+x$ direction at the velocity v_{III+} since region III contains nothing that could reflect the wave. Hence $G = 0$ and

$$\psi_{III} = \psi_{III+} = Fe^{ik_1x} \quad (5.50)$$

The transmission probability T for a particle to pass through the barrier is the ratio

Transmission probability

$$T = \frac{|\psi_{\text{III}+}|^2 v_{\text{III}+}}{|\psi_{\text{I}+}|^2 v_{\text{I}+}} = \frac{FF^* v_{\text{III}+}}{AA^* v_{\text{I}+}} \quad (5.51)$$

between the flux of particles that emerges from the barrier and the flux that arrives at it. In other words, T is the fraction of incident particles that succeed in tunneling through the barrier. Classically $T = 0$ because a particle with $E < U$ cannot exist inside the barrier; let us see what the quantum-mechanical result is.

In region II Schrödinger's equation for the particles is

$$\frac{d^2\psi_{\text{II}}}{dx^2} + \frac{2m}{\hbar^2}(E - U)\psi_{\text{II}} = 0 \quad (5.52)$$

Since $U > E$ the solution is

Wave function inside barrier

$$\psi_{\text{II}} = Ce^{-k_2 x} + De^{k_2 x} \quad k_2^2 \quad (5.53)$$

where the wave number inside the barrier is

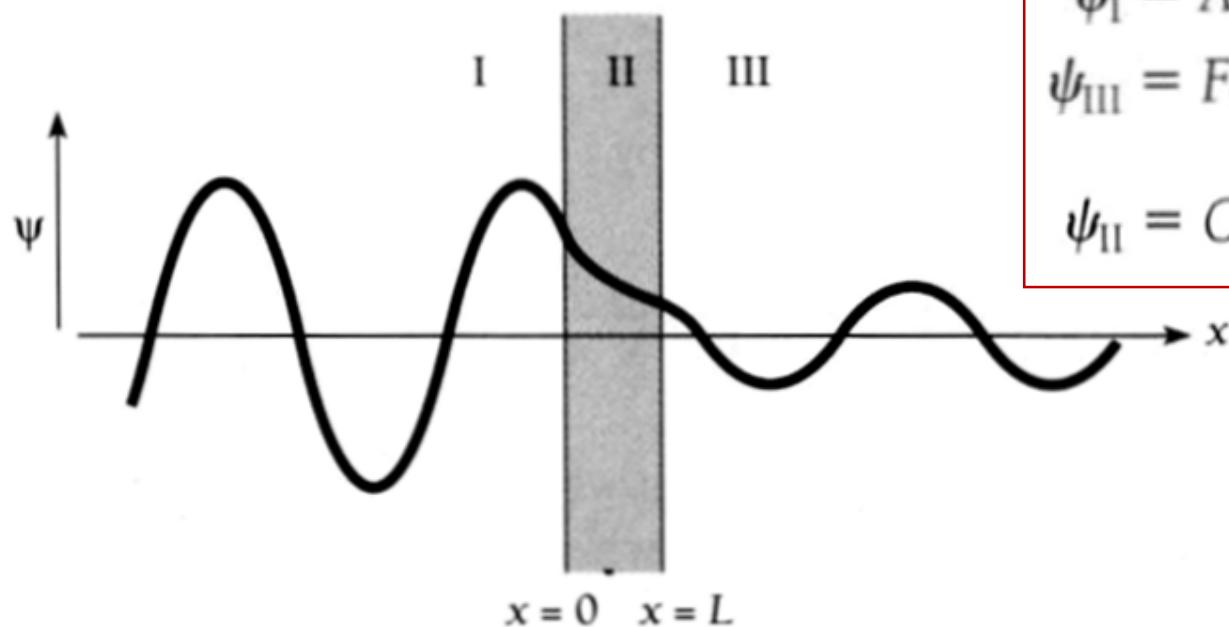
Wave number inside barrier

$$k_2 = \frac{\sqrt{2m(U - E)}}{\hbar} \quad (5.54)$$

Since the exponents are real quantities, ψ_{II} does not oscillate and therefore does not represent a moving particle. However, the probability density $|\psi_{\text{II}}|^2$ is not zero, so there is a finite probability of finding a particle within the barrier. Such a particle may emerge into region III or it may return to region I.

Applying the Boundary Conditions

In order to calculate the transmission probability T we have to apply the appropriate boundary conditions to ψ_I , ψ_{II} , and ψ_{III} . Figure 5.9 shows the wave functions in regions I, II, and III. As discussed earlier, both ψ and its derivative $\partial\psi/\partial x$ must be continuous everywhere. With reference to Fig. 5.9, these conditions mean that for a perfect fit at each side of the barrier, the wave functions inside and outside must have the same value and the same slope.



$$\psi_I = Ae^{ik_1 x} + Be^{-ik_1 x} \quad (5.43)$$

$$\psi_{III} = Fe^{ik_1 x} + \cancel{Ge^{-ik_1 x}} \quad (5.44)$$

$$\psi_{II} = Ce^{-k_2 x} + De^{k_2 x} \quad (5.53)$$

Figure 5.9 At each wall of the barrier, the wave functions inside and outside it must match up perfectly, which means that they must have the same values and slopes there.

$$\psi_I = Ae^{ik_1x} + Be^{-ik_1x} \quad (5.43)$$

$$\psi_{III} = Fe^{ik_1x} + Ge^{-ik_1x} \quad (5.44)$$

$$\psi_{II} = Ce^{-k_2x} + De^{k_2x} \quad (5.53)$$

Hence at the left-hand side of the barrier

$$\left. \begin{array}{l} \psi_I = \psi_{II} \\ \frac{d\psi_I}{dx} = \frac{d\psi_{II}}{dx} \end{array} \right\} x=0 \quad (5.56)$$

Boundary conditions
at $x = 0$

and at the right-hand side

$$\left. \begin{array}{l} \psi_{II} = \psi_{III} \\ \frac{d\psi_{II}}{dx} = \frac{d\psi_{III}}{dx} \end{array} \right\} x=L \quad (5.57)$$

Boundary conditions
at $x = L$

$$\left. \begin{array}{l} \psi_{II} = \psi_{III} \\ \frac{d\psi_{II}}{dx} = \frac{d\psi_{III}}{dx} \end{array} \right\} x=L \quad (5.58)$$

Now we substitute ψ_I , ψ_{II} , and ψ_{III} from Eqs. (5.43), (5.49), and (5.53) into the above equations. This yields in the same order

$$A + B = C + D \quad (5.59)$$

$$ik_1A - ik_1B = -k_2C + k_2D \quad (5.60)$$

$$Ce^{-k_2L} + De^{k_2L} = Fe^{ik_1L} \quad (5.61)$$

$$-k_2Ce^{-k_2L} + k_2De^{k_2L} = ik_1Fe^{ik_1L} \quad (5.62)$$

Equations (5.59) to (5.62) may be solved for (A/F) to give

$$\left(\frac{A}{F} \right) = \left[\frac{1}{2} + \frac{i}{4} \left(\frac{k_2}{k_1} - \frac{k_1}{k_2} \right) \right] e^{(ik_1+k_2)L} + \left[\frac{1}{2} - \frac{i}{4} \left(\frac{k_2}{k_1} - \frac{k_1}{k_2} \right) \right] e^{(ik_1-k_2)L} \quad (5.63)$$

Link

$$\left(\frac{A}{F}\right) = \left[\frac{1}{2} + \frac{i}{4} \left(\frac{k_2}{k_1} - \frac{k_1}{k_2} \right) \right] e^{(ik_1+k_2)L} + \left[\frac{1}{2} - \frac{i}{4} \left(\frac{k_2}{k_1} - \frac{k_1}{k_2} \right) \right] e^{(ik_1-k_2)L} \quad (5.63)$$

Let us assume that the potential barrier U is high relative to the energy E of the incident particles. If this is the case, then $k_2/k_1 > k_1/k_2$ and

$$\frac{k_2}{k_1} - \frac{k_1}{k_2} \approx \frac{k_2}{k_1} \quad (5.64)$$

Let us also assume that the barrier is wide enough for ψ_{II} to be severely weakened between $x = 0$ and $x = L$. This means that $k_2 L \gg 1$ and

$$e^{k_2 L} \gg e^{-k_2 L}$$

Hence Eq. (5.63) can be approximated by

$$\left(\frac{A}{F}\right) = \left(\frac{1}{2} + \frac{ik_2}{4k_1} \right) e^{(ik_1+k_2)L} = \left(\frac{1}{2} + \frac{ik_2}{4k_1} \right) e^{ik_1 L} e^{k_2 L} \quad (5.65)$$

The complex conjugate of (A/F) , which we need to compute the transmission probability T , is found by replacing i by $-i$ wherever it occurs in (A/F) :

$$\left(\frac{A}{F}\right)^* = \left(\frac{1}{2} - \frac{ik_2}{4k_1} \right) e^{(-ik_1+k_2)L} = \left(\frac{1}{2} - \frac{ik_2}{4k_1} \right) e^{-ik_1 L} e^{k_2 L} \quad (5.66)$$

Now we multiply (A/F) and $(A/F)^*$ to give $\frac{AA^*}{FF^*} = \left(\frac{1}{4} + \frac{k_2^2}{16k_1^2}\right)e^{2k_2 L}$

Here $v_{III+} = v_{I+}$ so $v_{III+}/v_{I+} = 1$ in Eq. (5.51), which means that the transmission probability is

Transmission probability $T = \frac{FF^*v_{III+}}{AA^*v_{I+}} = \left(\frac{AA^*}{FF^*}\right)^{-1} = \left[\frac{16}{4 + (k_2/k_1)^2}\right]e^{-2k_2 L}$ (5.67)

From the definitions of k_1 , Eq. (5.45), and of k_2 , Eq. (5.54), we see that

$$\left(\frac{k_2}{k_1}\right)^2 = \frac{2m(U - E)/\hbar^2}{2mE/\hbar^2} = \frac{U}{E} - 1 \quad (5.68)$$

This formula means that the quantity in brackets in Eq. (5.67) varies much less with E and U than does the exponential. The bracketed quantity, furthermore, always is of the order of magnitude of 1 in value. A reasonable approximation of the transmission probability is therefore

Approximate transmission probability

$$T = e^{-2k_2 L} \quad (5.69)$$

Example 5.5

Electrons with energies of 1.0 eV and 2.0 eV are incident on a barrier 10.0 eV high and 0.50 nm wide. (a) Find their respective transmission probabilities. (b) How are these affected if the barrier is doubled in width?

Solution

(a) For the 1.0-eV electrons

$$k_2 = \frac{\sqrt{2m(U - E)}}{\hbar}$$
$$= \frac{\sqrt{(2)(9.1 \times 10^{-31} \text{ kg})[(10.0 - 1.0) \text{ eV}](1.6 \times 10^{-19} \text{ J/eV})}}{1.054 \times 10^{-34} \text{ J}\cdot\text{s}}$$
$$= 1.6 \times 10^{10} \text{ m}^{-1}$$

Since $L = 0.50 \text{ nm} = 5.0 \times 10^{-10} \text{ m}$, $2k_2L = (2)(1.6 \times 10^{10} \text{ m}^{-1})(5.0 \times 10^{-10} \text{ m}) = 16$, and the approximate transmission probability is

$$T_1 = e^{-2k_2L} = e^{-16} = 1.1 \times 10^{-7}$$

One 1.0-eV electron out of 8.9 million can tunnel through the 10-eV barrier on the average. For the 2.0-eV electrons a similar calculation gives $T_2 = 2.4 \times 10^{-7}$. These electrons are over twice as likely to tunnel through the barrier.

(b) If the barrier is doubled in width to 1.0 nm, the transmission probabilities become

$$T'_1 = 1.3 \times 10^{-14} \quad T'_2 = 5.1 \times 10^{-14}$$

Evidently T is more sensitive to the width of the barrier than to the particle energy here.

Scanning Tunneling Microscope

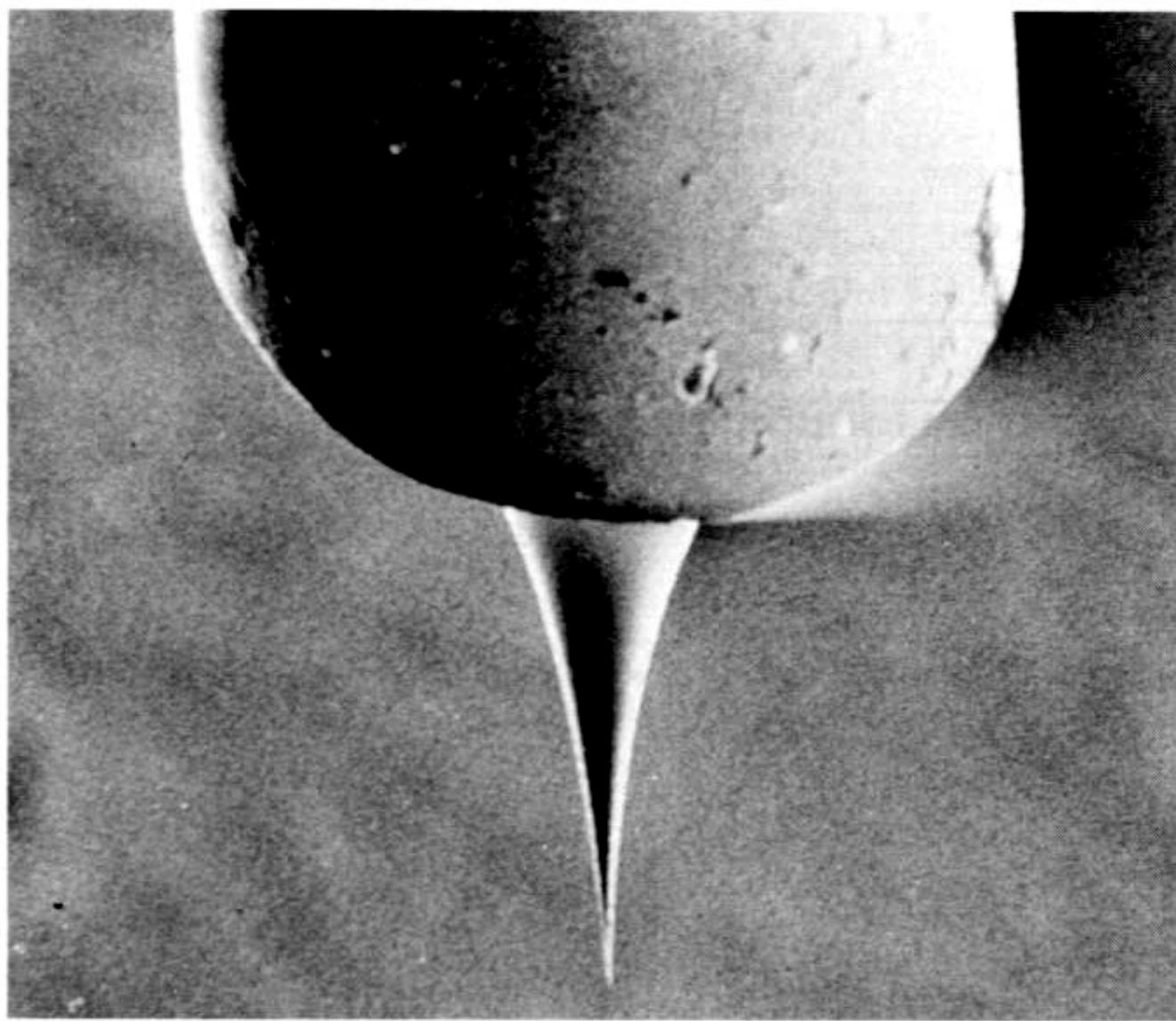
The ability of electrons to tunnel through a potential barrier is used in an ingenious way in the **scanning tunneling microscope** (STM) to study surfaces on an atomic scale of size. The STM was invented in 1981 by Gert Binning and Heinrich Rohrer, who shared the 1986 Nobel Prize in physics with Ernst Ruska, the inventor of the electron microscope. In an STM, a metal probe with a point so fine that its tip is a single atom is brought close to the surface of a conducting or semiconducting material. Normally even the most loosely bound electrons in an atom on a surface need several electron-volts of energy to escape—this is the work function discussed in Chap. 2 in connection with the photoelectric effect. However, when a voltage of only 10 mV or so is applied between the probe and the surface, electrons can tunnel across the gap between them if the gap is small enough, a nanometer or two.

Scanning Tunneling Microscope

According to Eq. (5.69) the electron transmission probability is proportional to e^{-L} , where L is the gap width, so even a small change in L (as little as 0.01 nm, less than a twentieth the diameter of most atoms) means a detectable change in the tunneling current. What is done is to move the probe across the surface in a series of closely spaced back-and-forth scans in about the same way an electron beam traces out an image on the screen of a television picture tube. The height of the probe is continually adjusted to give a constant tunneling current, and the adjustments are recorded so that a map of surface height versus position is built up. Such a map is able to resolve individual atoms on a surface.

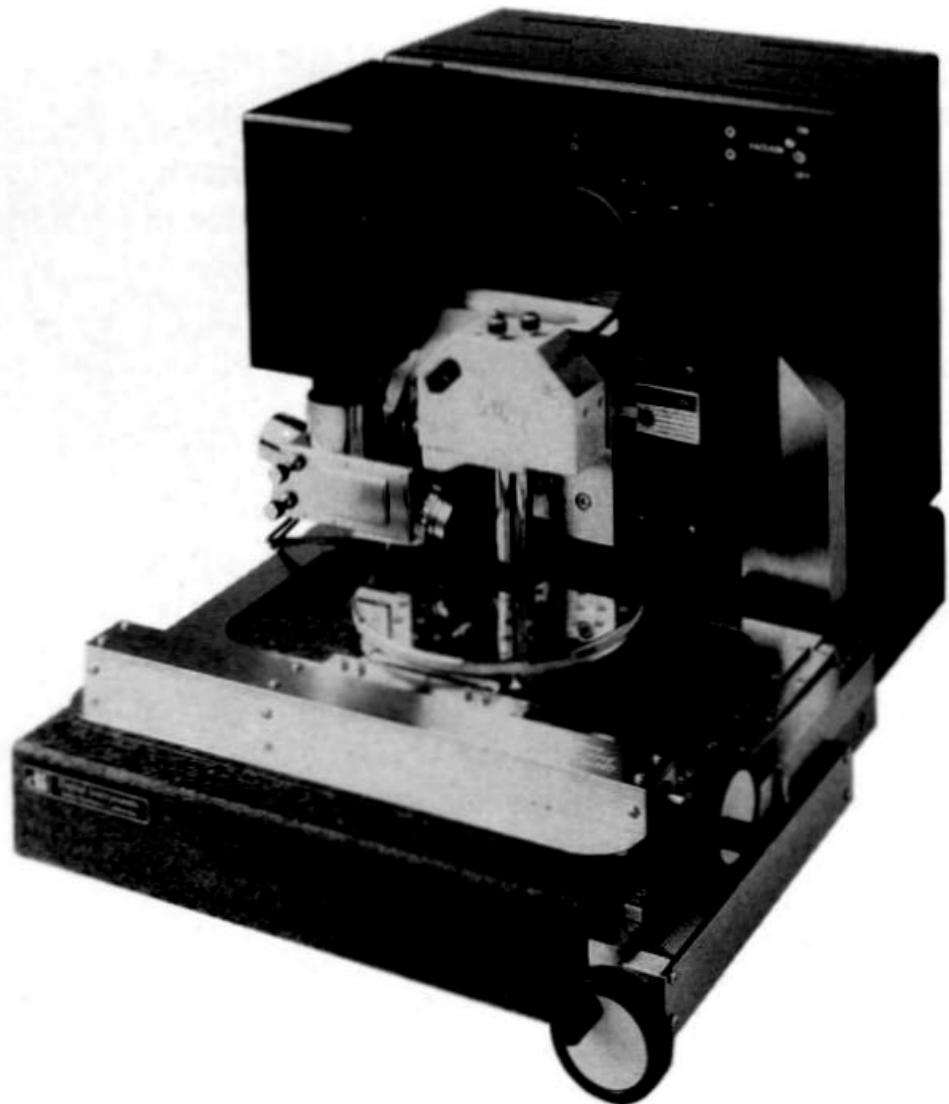
How can the position of the probe be controlled precisely enough to reveal the outlines of individual atoms? The thickness of certain ceramics changes when a voltage is applied across them, a property called **piezoelectricity**. The changes might be several tenths of a nanometer per volt. In an STM, piezoelectric controls move the probe in x and y directions across a surface and in the z direction perpendicular to the surface.

Actually, the result of an STM scan is not a true topographical map of surface height but a contour map of constant electron density on the surface. This means that atoms of different elements appear differently, which greatly increases the value of the STM as a research tool.



The tungsten probe of a scanning tunneling microscope. (IBM Research)

Although many biological materials conduct electricity, they do so by the flow of ions rather than of electrons and so cannot be studied with STMs. A more recent development, the **atomic force microscope** (AFM) can be used on any surface, although with somewhat less resolution than an STM. In an AFM, the sharp tip of a fractured diamond presses gently against the atoms on a surface. A spring keeps the pressure of the tip constant, and a record is made of the deflections of the tip as it moves across the surface. The result is a map showing contours of constant repulsive force between the electrons of the probe and the electrons of the surface atoms. Even relatively soft biological materials can be examined with an AFM and changes in them monitored. For example, the linking together of molecules of the blood protein fibrin, which occurs when blood clots, has been watched with an AFM.



Atomic force microscope. (Courtesy Digital Instruments)



Nerve cell growth cone imaged with an atomic force microscope. The width of the scan is 42 μm .
(Courtesy Digital Instruments)

5.9 HARMONIC OSCILLATOR

Its energy levels are evenly spaced

Harmonic motion takes place when a system of some kind vibrates about an equilibrium configuration. The system may be an object supported by a spring or floating in a liquid, a diatomic molecule, an atom in a crystal lattice—there are countless examples on all scales of size. The condition for harmonic motion is the presence of a restoring force that acts to return the system to its equilibrium configuration when it is disturbed. The inertia of the masses involved causes them to overshoot equilibrium, and the system oscillates indefinitely if no energy is lost.

In the special case of simple harmonic motion, the restoring force F on a particle of mass m is linear; that is, F is proportional to the particle's displacement x from its equilibrium position and in the opposite direction. Thus

Hooke's law

$$F = -kx \quad (5.70)$$

Hooke's law

$$F = -kx \quad (5.70)$$

This relationship is customarily called Hooke's law. From the second law of motion, $F = ma$, we have

$$\begin{aligned} -kx &= m \frac{d^2x}{dt^2} \\ \frac{d^2x}{dt^2} + \frac{k}{m}x &= 0 \end{aligned} \quad (5.71)$$

Harmonic oscillator

There are various ways to write the solution to Eq. (5.71). A common one is

$$x = A \cos(2\pi\nu t + \phi) \quad (5.72)$$

where

Frequency of harmonic oscillator

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad (5.73)$$

is the frequency of the oscillations and A is their amplitude. The value of ϕ , the phase angle, depends upon what x is at the time $t = 0$.

The importance of the simple harmonic oscillator in both classical and modern physics lies not in the strict adherence of actual restoring forces to Hooke's law, which is seldom true, but in the fact that these restoring forces reduce to Hooke's law for small displacements x . As a result, any system in which something executes small vibrations about an equilibrium position behaves very much like a simple harmonic oscillator.

To verify this important point, we note that any restoring force which is a function of x can be expressed in a Maclaurin's series about the equilibrium position $x = 0$ as

$$F(x) = F_{x=0} + \left(\frac{dF}{dx}\right)_{x=0} x + \frac{1}{2}\left(\frac{d^2F}{dx^2}\right)_{x=0} x^2 + \frac{1}{6}\left(\frac{d^3F}{dx^3}\right)_{x=0} x^3 + \dots$$

Since $x = 0$ is the equilibrium position, $F_{x=0} = 0$. For small x the values of x^2, x^3, \dots are very small compared with x , so the third and higher terms of the series can be neglected. The only term of significance when x is small is therefore the second one. Hence

$$F(x) = \left(\frac{dF}{dx}\right)_{x=0} x$$

which is Hooke's law when $(dF/dx)_{x=0}$ is negative, as of course it is for any restoring force. The conclusion, then, is that *all* oscillations are simple harmonic in character when their amplitudes are sufficiently small.

The potential-energy function $U(x)$ that corresponds to a Hooke's law force may be found by calculating the work needed to bring a particle from $x = 0$ to $x = x$ against such a force. The result is

$$U(x) = - \int_0^x F(x) dx = k \int_0^x x dx = \frac{1}{2} kx^2 \quad (5.74)$$

which is plotted in Fig. 5.10. The curve of $U(x)$ versus x is a parabola. If the energy of the oscillator is E , the particle vibrates back and forth between $x = -A$ and $x = +A$, where E and A are related by $E = \frac{1}{2}kA^2$. Figure 8.18 shows how a nonparabolic potential energy curve can be approximated by a parabola for small displacements.

Figure 5.10

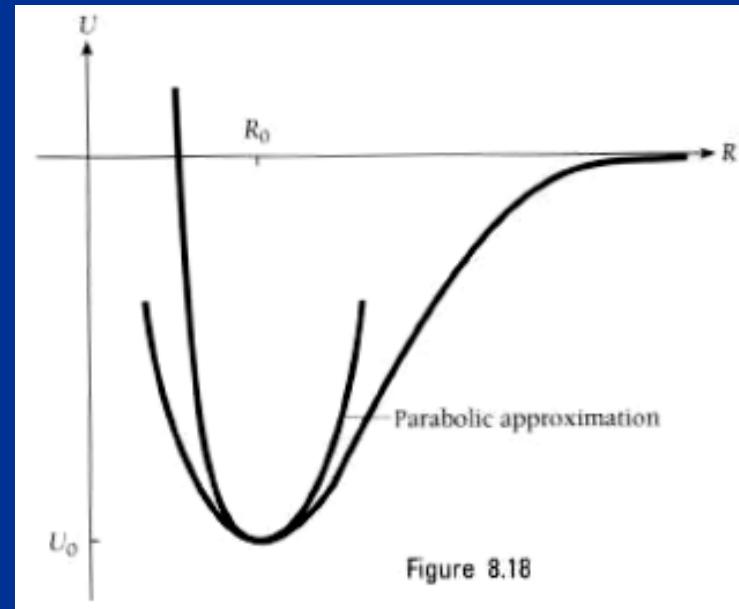
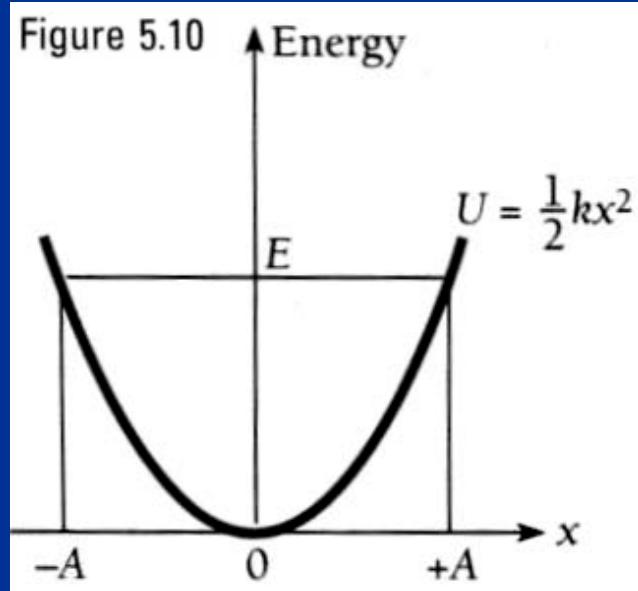


Figure 8.18

Even before we make a detailed calculation we can anticipate three quantum-mechanical modifications to this classical picture:

- 1 The allowed energies will not form a continuous spectrum but instead a discrete spectrum of certain specific values only.
- 2 The lowest allowed energy will not be $E = 0$ but will be some definite minimum $E = E_0$.
- 3 There will be a certain probability that the particle can penetrate the potential well it is in and go beyond the limits of $-A$ and $+A$.

Energy Levels

Schrödinger's equation for the harmonic oscillator is, with $U = \frac{1}{2}kx^2$,

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} \left(E - \frac{1}{2}kx^2 \right) \psi = 0 \quad (5.75)$$

It is convenient to simplify Eq. (5.75) by introducing the dimensionless quantities

$$y = \left(\frac{1}{\hbar} \sqrt{km} \right)^{1/2} x = \sqrt{\frac{2\pi m\nu}{\hbar}} x \quad (5.76)$$

and

$$\alpha = \frac{2E}{\hbar} \sqrt{\frac{m}{k}} = \frac{2E}{\hbar\nu} \quad (5.77)$$

where ν is the classical frequency of the oscillation given by Eq. (5.73). In making these substitutions, what we have done is change the units in which x and E are expressed from meters and joules, respectively, to dimensionless units.

In terms of y and α Schrödinger's equation becomes

$$\frac{d^2\psi}{dy^2} + (\alpha - y^2)\psi = 0 \quad (5.78)$$

The solutions to this equation that are acceptable here are limited by the condition that $\psi \rightarrow 0$ as $y \rightarrow \infty$ in order that

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

Otherwise the wave function cannot represent an actual particle.

$$\frac{d^2\psi}{dy^2} + (\alpha - y^2)\psi = 0$$

The mathematical properties of Eq. (5.78) are such that this condition will be fulfilled only when

$$\alpha = 2n + 1 \quad n = 0, 1, 2, 3, \dots$$

Since $\alpha = 2E/h\nu$ according to Eq. (5.77), the energy levels of a harmonic oscillator whose classical frequency of oscillation is ν are given by the formula

Energy levels of harmonic oscillator $E_n = (n + \frac{1}{2})h\nu \quad n = 0, 1, 2, 3, \dots$ (5.79)

The energy of a harmonic oscillator is thus quantized in steps of $h\nu$.

We note that when $n = 0$,

Zero-point energy $E_0 = \frac{1}{2}h\nu$ (5.80)

which is the lowest value the energy of the oscillator can have. This value is called the **zero-point energy** because a harmonic oscillator in equilibrium with its surroundings would approach an energy of $E = E_0$ and not $E = 0$ as the temperature approaches 0 K.

Figure 5.11 is a comparison of the energy levels of a harmonic oscillator with those of a hydrogen atom and of a particle in a box with infinitely hard walls. The shapes of the respective potential-energy curves are also shown. The spacing of the energy levels is constant only for the harmonic oscillator.

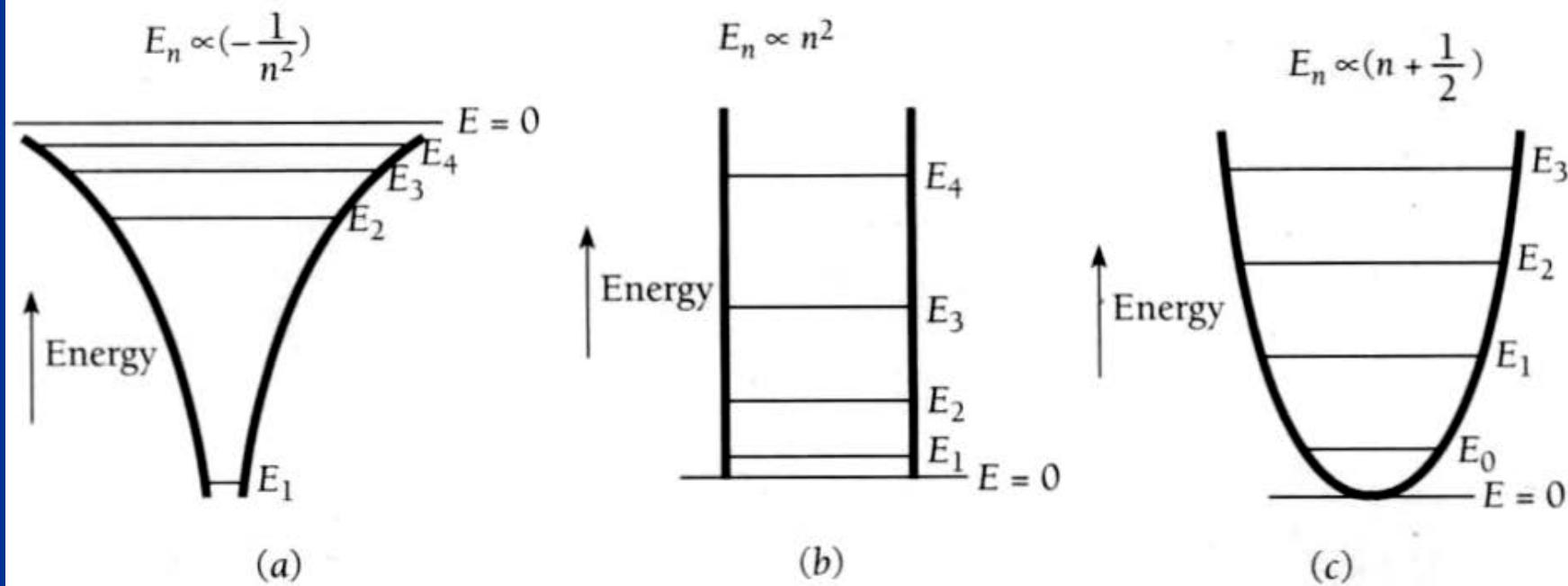


Figure 5.11 Potential wells and energy levels of (a) a hydrogen atom, (b) a particle in a box, and (c) a harmonic oscillator. In each case the energy levels depend in a different way on the quantum number n . Only for the harmonic oscillator are the levels equally spaced. The symbol \propto means “is proportional to.”

Wave Functions

For each choice of the parameter α_n there is a different wave function ψ_n . Each function consists of a polynomial $H_n(y)$ (called a **Hermite polynomial**) in either odd or even powers of y , the exponential factor $e^{-y^2/2}$, and a numerical coefficient which is needed for ψ_n to meet the normalization condition

$$\int_{-\infty}^{\infty} |\psi_n|^2 dy = 1 \quad n = 0, 1, 2 \dots$$

The general formula for the n th wave function is

Harmonic oscillator

$$\psi_n = \left(\frac{2m\nu}{\hbar} \right)^{1/4} (2^n n!)^{-1/2} H_n(y) e^{-y^2/2} \quad (5.81)$$

Harmonic oscillator

$$\psi_n = \left(\frac{2m\nu}{\hbar} \right)^{1/4} (2^n n!)^{-1/2} H_n(y) e^{-y^2/2} \quad (5.81)$$

The first six Hermite polynomials $H_n(y)$ are listed in Table 5.1.

TABLE 5.1 Some Hermite Polynomials

<i>n</i>	$H_n(y)$	α_n	E_n
0	1	1	$\frac{1}{2}\hbar\nu$
1	$2y$	3	$\frac{3}{2}\hbar\nu$
2	$4y^2 - 2$	5	$\frac{5}{2}\hbar\nu$
3	$8y^3 - 12y$	7	$\frac{7}{2}\hbar\nu$
4	$16y^4 - 48y^2 + 12$	9	$\frac{9}{2}\hbar\nu$
5	$32y^5 - 160y^3 + 120y$	11	$\frac{11}{2}\hbar\nu$

The wave functions that correspond to the first six energy levels of a harmonic oscillator are shown in Fig. 5.12. In each case the range to which a particle oscillating classically with the same total energy E_n would be confined is indicated. Evidently the particle is able to penetrate into classically forbidden regions—in other words, to exceed the amplitude A determined by the energy—with an exponentially decreasing probability, just as in the case of a particle in a finite square potential well.

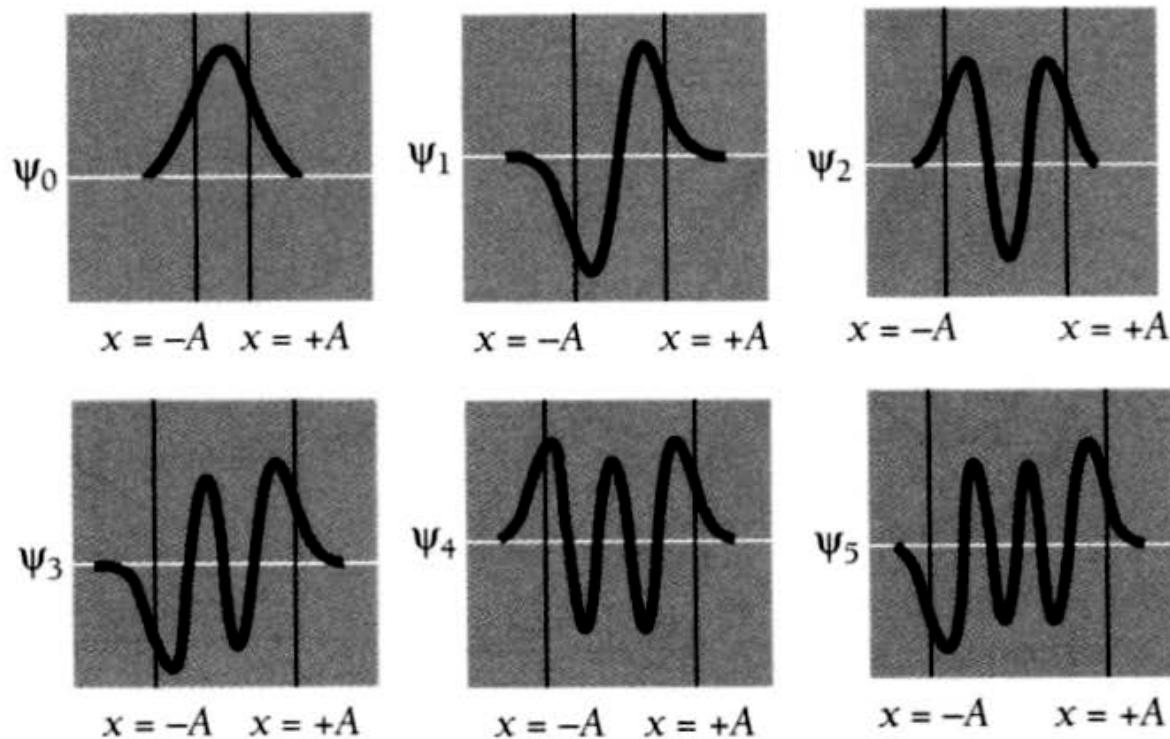


Figure 5.12 The first six harmonic-oscillator wave functions. The vertical lines show the limits $-A$ and $+A$ between which a classical oscillator with the same energy would vibrate.

It is interesting and instructive to compare the probability densities of a classical harmonic oscillator and a quantum-mechanical harmonic oscillator of the same energy. The upper curves in Fig. 5.13 show this density for the classical oscillator. The probability P of finding the particle at a given position is greatest at the endpoints of its motion, where it moves slowly, and least near the equilibrium position ($x = 0$), where it moves rapidly.

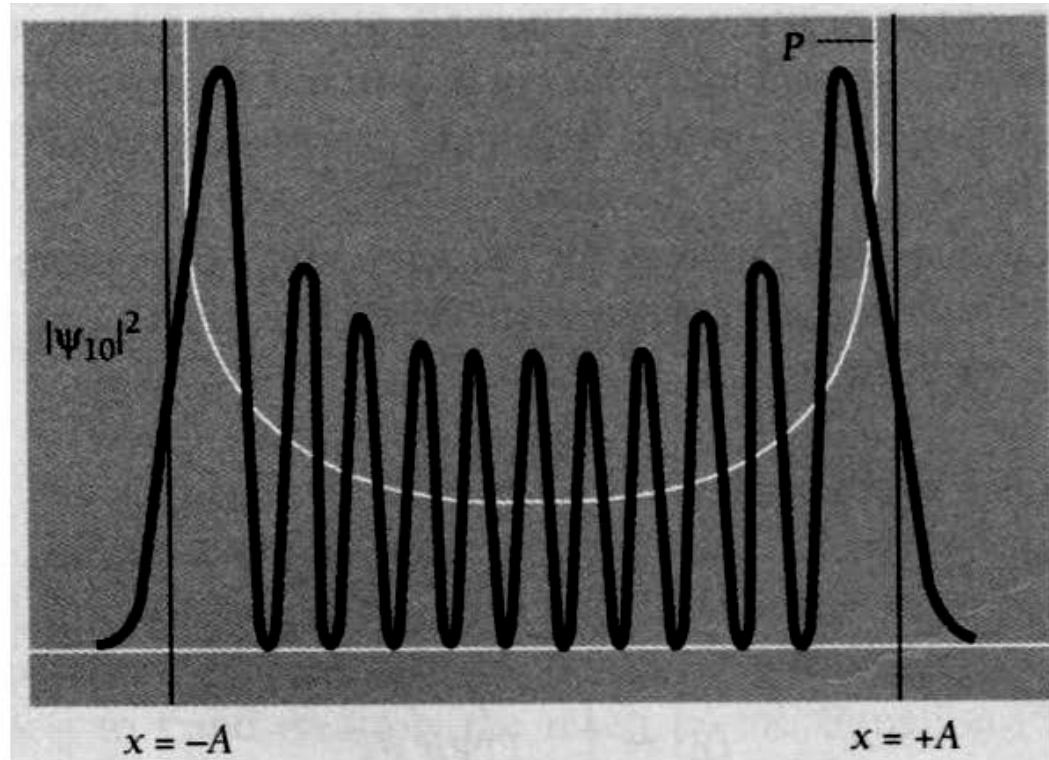
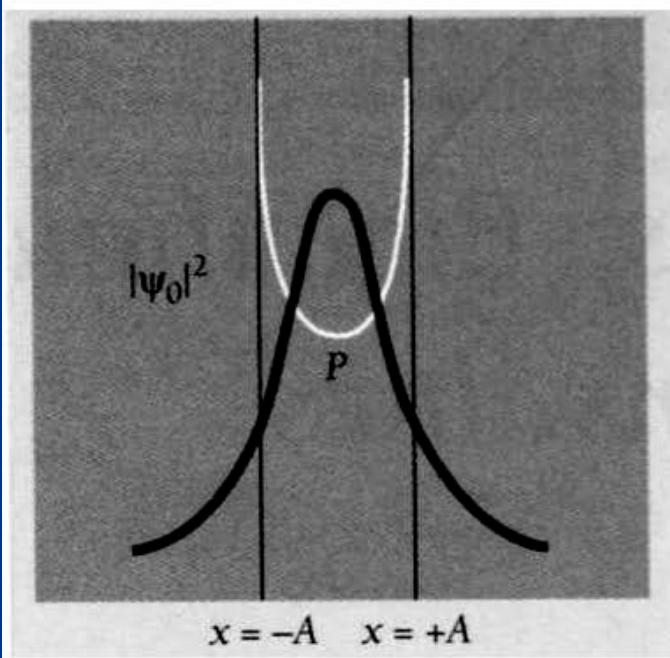


Figure 5.13 Probability densities for the $n = 0$ and $n = 10$ states of a quantum-mechanical harmonic oscillator. The probability densities for classical harmonic oscillators with the same energies are shown in white. In the $n = 10$ state, the wavelength is shortest at $x = 0$ and longest at $x = -A$.

Exactly the opposite behavior occurs when a quantum-mechanical oscillator is in its lowest energy state of $n = 0$. As shown, the probability density $|\psi_0|^2$ has its maximum value at $x = 0$ and drops off on either side of this position. However, this disagreement becomes less and less marked with increasing n . The lower graph of Fig. 5.13 corresponds to $n = 10$, and it is clear that $|\psi_{10}|^2$ when averaged over x has approximately the general character of the classical probability P . This is another example of the correspondence principle mentioned in Chap. 4: In the limit of large quantum numbers, quantum physics yields the same results as classical physics.

It might be objected that although $|\psi_{10}|^2$ does indeed approach P when smoothed out, nevertheless $|\psi_{10}|^2$ fluctuates rapidly with x whereas P does not. However, this objection has meaning only if the fluctuations are observable, and the smaller the spacing of the peaks and hollows, the more difficult it is to detect them experimentally. The exponential “tails” of $|\psi_{10}|^2$ beyond $x = \pm A$ also decrease in magnitude with increasing n . Thus the classical and quantum pictures begin to resemble each other more and more the larger the value of n , in agreement with the correspondence principle, although they are very different for small n .

In general, expectation value for any observable quantity is found by putting the quantum mechanical operator for that observable in the integral of the wavefunction over space:

$$\langle Q \rangle = \int_{-\infty}^{\infty} \psi^* Q_{operator} \psi dV$$

integral over
all space

Operators in Quantum Mechanics

Associated with each measurable parameter in a physical system is a quantum mechanical operator.

Such operators arise because in quantum mechanics you are describing nature with waves (mathematically, the wavefunction) rather than with discrete particles whose motion and dynamics can be described with the deterministic equations of Newtonian physics.

Part of the development of quantum mechanics is the establishment of operators associated with the parameters needed to describe the system. Some of those operators are listed below.

$f(x)$	Any function of position, such as x , or potential $V(x)$	$f(x)$
p_x	x component of momentum (y and z same form)	$\frac{\hbar}{i} \frac{\partial}{\partial x}$
E	Hamiltonian (time independent)	$\frac{p_{op}^2}{2m} + V(x)$
E	Hamiltonian (time dependent)	$i\hbar \frac{\partial}{\partial t}$
KE	Kinetic energy	$\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$
L_z	z component of angular momentum	$-i\hbar \frac{\partial}{\partial \phi}$

$|\psi|^2 \propto$ probability of finding an electron at an particular location

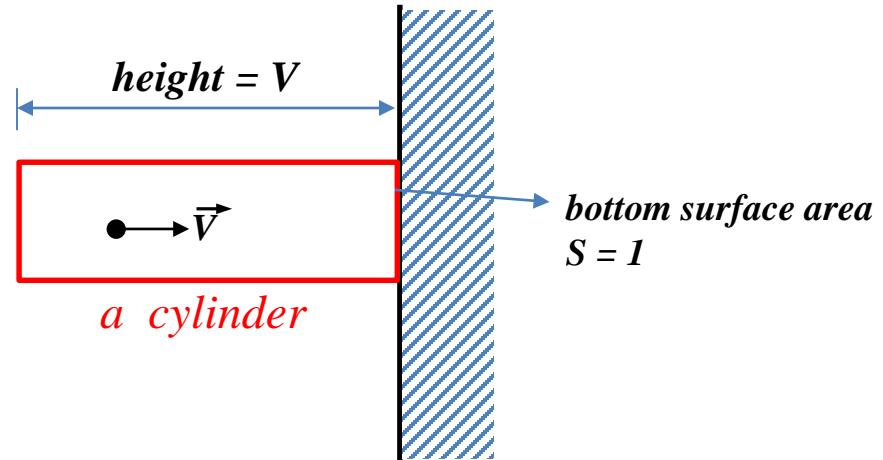
\propto for many electrons, percentage of electrons at this location
i.e. the density of the electrons (numbers of electron/unit volume)

The volume of the cylinder:

$$V \cdot S \text{ (height} \times \text{area)}$$

The numbers of electrons in the cylinder:

$$|\psi|^2 V \cdot S \text{ (density} \times \text{volume)}$$



For unit area, $S=1$

$$|\psi|^2 V \cdot S = |\psi|^2 V$$

In 1 second, all the electrons in the cylinder will pass through the bottom surface, because the cylinder height is V (i.e. the distance of electrons will go in 1 second).

So, $|\psi|^2 V =$ **the numbers of electrons passing unit area per second**

$$A + B = C + D$$

$$ik_1 A - ik_1 B = -k_2 C + k_2 D$$

$$\Rightarrow 2A = \left[1 - \frac{k_2}{ik_1}\right]C + \left[1 + \frac{k_2}{ik_1}\right]D$$

$$A = \frac{1}{2} \left[1 + \frac{ik_2}{k_1}\right]C + \frac{1}{2} \left[1 - \frac{ik_2}{k_1}\right]D \quad (1)$$

$$Ce^{-k_2 L} + De^{k_2 L} = Fe^{ik_1 L}$$

$$-k_2 Ce^{-k_2 L} + k_2 De^{k_2 L} = ik_1 Fe^{ik_1 L}$$



$$2Ce^{-k_2 L} = \left[1 - \frac{ik_1}{k_2}\right]Fe^{ik_1 L}$$

$$\rightarrow C = \frac{1}{2} \left[1 - \frac{ik_1}{k_2}\right]Fe^{(ik_1+k_2)L} \quad (3)$$

Substitute (2) & (3) into (1):

$$A = \frac{1}{4} \left[1 + \frac{ik_2}{k_1}\right] \left[1 - \frac{ik_1}{k_2}\right] Fe^{(ik_1+k_2)L} + \frac{1}{4} \left[1 - \frac{ik_2}{k_1}\right] \left[1 + \frac{ik_1}{k_2}\right] Fe^{(ik_1-k_2)L}$$

$$\frac{A}{F} = \frac{1}{4} \left[1 - \frac{ik_1}{k_2} + \frac{ik_2}{k_1} + 1\right] e^{(ik_1+k_2)L} + \frac{1}{4} \left[1 + \frac{ik_1}{k_2} - \frac{ik_2}{k_1} + 1\right] e^{(ik_1-k_2)L}$$

$$\frac{A}{F} = \frac{1}{4} \left[1 - \frac{ik_1}{k_2} + \frac{ik_2}{k_1} + 1 \right] e^{(ik_1+k_2)L} + \frac{1}{4} \left[1 + \frac{ik_1}{k_2} - \frac{ik_2}{k_1} + 1 \right] e^{(ik_1-k_2)L}$$

$$\frac{A}{F} = \left[\frac{1}{2} + \frac{i}{4} \left(\frac{k_2}{k_1} - \frac{k_1}{k_2} \right) \right] e^{(ik_1+k_2)L} + \left[\frac{1}{2} - \frac{i}{4} \left(\frac{k_2}{k_1} - \frac{k_1}{k_2} \right) \right] e^{(ik_1-k_2)L} \quad (5.63)$$

Return