Solutions of Time-Independent Schroedinger Equations

6

6-1 Introduction

In this chapter we shall obtain many interesting predictions concerning quantum mechanical phenomena. We shall also discuss some of the experiments confirming the predictions, and some of the important practical applications of the phenomena. The predictions will be obtained by solving the time-independent Schroedinger equation for different forms of the potential energy function $V(x)$, to find the eigenfunctions, eigenvalues, and wave functions, and then using the procedures developed in the previous chapter to interpret the physical significance of these quantities.

Our approach will be very systematic. We shall start by treating the simplest possible form of the potential, namely $V(x) = 0$. Then we shall gradually add complexity to the potential. With each new potential treated, the student will obtain new insight into quantum mechanics and into the behavior of microscopic systems. In this process the student should begin to develop an intuition for quantum mechanics, just as he has developed an intuition for classical mechanics by repeated use of that theory.

The potentials considered in the first sections of this chapter are not able to bind a particle because there is no region in which they have a depression. Although discrete quantization of energy will not be found for these potentials, other fundamental phenomena will be found. In addition to the fact that they naturally fit in at the beginning of our systematic approach, another reason for treating nonbinding potentials first is that it emphasizes their importance. Probably half of the work *currently* being done in quantum mechanics concerns unbound particles.

It is true, however, that most of the applications of quantum mechanics that were made *initially* concerned bound particles. Most aspects of the structure of atoms, molecules, and solids are examples of bound particle problems, as are many aspects of nuclear structure. Since these are the topics we shall concentrate on in the following chapters of this book, some students (or instructors) may prefer to go directly to Section 6-7, which is the first to treat binding potentials, or to Section 6-8, which treats an important special case. Those sections are sufficiently self-contained to make such short cuts feasible without too much difficulty.

Throughout this chapter we deal only with time-independent potentials, since only for such potentials does the time-independent Schroedinger equation have significance. We further restrict ourselves to a single dimension because this simplifies the mathematics while still allowing us to demonstrate most of the interesting quantum phenomena. Obvious exceptions are phenomena involving angular momentum, since this quantity has no meaning in one dimension. Because angular momentum plays a dominant role in atomic structure, the following chapter begins by extending our development of quantum mechanics to three dimensions.

6-2 The Zero Potential

The simplest time-independent Schroedinger equation is the one for the case: $V(x) =$ const. A particle moving under the influence of such a potential is a *free particle* since the force acting on it is $F = -dV(x)/dx = 0$. As this is true regardless of the value of the constant, we do not lose generality by choosing the arbitrary additive constant, that always arises in the definition of a potential energy, in such a way as to obtain

$$V(x) = 0 \tag{6-1}$$

We know that in *classical mechanics* a free particle may be either at rest or moving with constant momentum p. In either case its total energy E is a constant.

To find the behavior predicted by *quantum mechanics* for a free particle, we solve the time-independent Schroedinger equation, (5-43), setting $V(x) = 0$. With this form for the potential, the equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x) \tag{6-2}$$

The solutions are the eigenfunctions $\psi(x)$, and the wave functions $\Psi(x,t)$ according to (5-44) are

$$\Psi(x,t) = \psi(x)e^{-iEt/\hbar} \tag{6-3}$$

The eigenvalues E are equal to the total energy of the particle. From the qualitative discussion of Section 5-7, we know that an acceptable solution of the time-independent Schroedinger equation for this nonbinding potential should exist for *any* value of $E \geq 0$.

Of course, we already know a form of the free particle wave function from our plausibility argument leading to the Schroedinger equation. That wave function, (5-23), is

$$\Psi(x,t) = \cos(kx - \omega t) + i\sin(kx - \omega t)$$

Rewriting it as a complex exponential, we have

$$\Psi(x,t) = e^{i(kx-\omega t)} \tag{6-4a}$$

The wave number k and angular frequency ω are

$$k = \frac{p}{\hbar} = \frac{\sqrt{2mE}}{\hbar} \quad \text{and} \quad \omega = \frac{E}{\hbar} \tag{6-4b}$$

We break the exponential into the product of two factors

$$\Psi(x,t) = e^{ikx}e^{-i\omega t} = e^{ikx}e^{-iEt/\hbar}$$

Then we compare with the general form of the wave function quoted in (6-3)

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

This comparison makes it apparent that

$$\psi(x) = e^{ikx} \qquad \text{where } k = \frac{\sqrt{2mE}}{\hbar} \tag{6-5}$$

That is, the complex exponential of (6-5) gives the form of a free particle eigenfunction corresponding to the eigenvalue E.

More specifically, it is a traveling wave free particle eigenfunction because the corresponding wave function, $\Psi(x,t) = e^{i(kx-\omega t)}$, represents a traveling wave. This can be seen, for example, from the fact that the nodes of the real part of the oscillatory wave function are located at positions where $kx - \omega t = (n + 1/2)\pi$, with $n = 0, \pm 1, \pm 2, \ldots$. The reason is that the real part of $\Psi(x,t)$, which is $\cos(kx - \omega t)$, has the value zero wherever $kx - \omega t = (n + 1/2)\pi$. Thus the nodes occur wherever

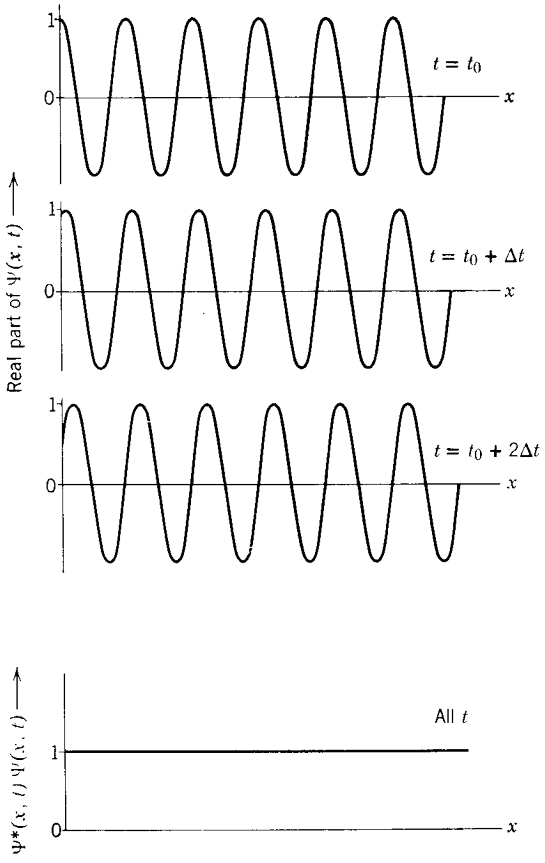

FIGURE 6-1

Top: The real part, $\cos(kx - \omega t)$, of a complex exponential traveling wave function, $\Psi = e^{i(kx-\omega t)}$, for a free particle. With increasing time the nodes move in the direction of increasing x. *Bottom:* For this wave function a sense of motion is not conveyed by plotting the probability density $\Psi^*\Psi = e^{-i(kx-\omega t)}e^{i(kx-\omega t)} = 1$ since it is constant for all t (and all x). Of course, we cannot plot Ψ itself, as it is complex.

$x = (n + 1/2)\pi/k + \omega t/k$ and, since these values of x increase with increasing t, the nodes travel in the direction of increasing x. The conclusion is illustrated in the top part of Figure 6-1 which shows plots of the real part of $\Psi(x,t)$ at successively later times. For this wave function, the probability density $\Psi^*(x,t)\Psi(x,t)$, illustrated in the bottom of Figure 6-1, conveys no sense of motion.

Intuition suggests that, for the same value of E, there should also be a wave function representing a wave traveling in the direction of decreasing x. The preceding argument indicates that this wave function would be written with the sign of kx reversed, that is

$$\Psi(x,t) = e^{i(-kx-\omega t)} \tag{6-6}$$

The corresponding eigenfunction would be

$$\psi(x) = e^{-ikx} \qquad \text{where } k = \frac{\sqrt{2mE}}{\hbar} \tag{6-7}$$

It is easy to see that this eigenfunction is also a solution to the time-independent Schroedinger equation for $V(x) = 0$. In fact, any arbitrary linear combination of the two eigenfunctions of (6-5) and (6-7), for the *same* value of the total energy E, is also a solution to the equation. To prove these statements, we take the linear combination

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \qquad \text{where } k = \frac{\sqrt{2mE}}{\hbar} \tag{6-8}$$

in which A and B are arbitrary constants, and substitute it into the time-independent Schroedinger equation, (6-2). Since

$$\frac{d^2\psi(x)}{dx^2} = i^2k^2Ae^{ikx} + i^2k^2Be^{-ikx} = -k^2\psi(x) = -\frac{2mE}{\hbar^2}\psi(x)$$

substitution into the equation yields

$$-\frac{\hbar^2}{2m}\left(-\frac{2mE}{\hbar^2}\right)\psi(x) = E\psi(x)$$

Since this is obviously satisfied, the linear combination is a valid solution to the time-independent Schroedinger equation.

The most general form of the solution to an ordinary (i.e., not partial) differential equation involving a second derivative contains two arbitrary constants. The reason is that obtaining the solution from such an equation basically amounts to performing two successive integrations to remove the second derivative, and each step yields a constant of integration. Examples familiar to the student are found in general solutions of Newton's equation of motion, which involve two arbitrary constants such as initial position and velocity. Since the linear combination of (6-8) is a solution containing two arbitrary constants to (6-2), it is its *general* solution. The general solution is useful because it allows us to describe *any* possible eigenfunction associated with the eigenvalue E. For instance, if we set $B = 0$, we obtain an eigenfunction for a wave traveling in the direction of increasing x. If we set $A = 0$, the wave is traveling in the direction of decreasing x. If we set $|A| = |B|$, there are two oppositely directed traveling waves that combine to form a standing wave. Standing wave eigenfunctions will be used in Section 6-3.

Let us consider now the question of giving physical interpretation to the free particle eigenfunctions and wave functions. Take first the case of a wave traveling in the direction of increasing x. The eigenfunction and wave function for this case are

$$\psi(x) = Ae^{ikx} \quad \text{and} \quad \Psi(x,t) = Ae^{i(kx-\omega t)} \tag{6-9}$$

An obvious guess is that the particle whose motion is described by these functions is also traveling in the direction of increasing x. To verify this, let us calculate the expectation value of the momentum, $\bar{p}$, for the particle. According to the general expectation value formula, (5-34)

$$\bar{p} = \int_{-\infty}^{\infty} \Psi^* p_{\text{op}} \Psi \, dx$$

where the operator for momentum is

$$p_{\text{op}} = -i\hbar\frac{\partial}{\partial x}$$

Now, for the wave function in question, we have

$$p_{\text{op}}\Psi = -i\hbar\frac{\partial}{\partial x}Ae^{i(kx-\omega t)} = -i\hbar(ik)Ae^{i(kx-\omega t)} = +\hbar k\Psi = +\sqrt{2mE}\,\Psi$$

so

$$\bar{p} = +\int_{-\infty}^{\infty} \Psi^*\sqrt{2mE}\,\Psi \, dx = +\sqrt{2mE}\int_{-\infty}^{\infty} \Psi^*\Psi \, dx$$

The integral on the right is the probability density integrated over the entire range of the x axis. This is just the probability that the particle will be found *somewhere*, which must equal one. Therefore, we obtain

$$\bar{p} = +\sqrt{2mE}$$

This is exactly the momentum that we would expect for a particle moving in the direction of increasing x with total energy E in a region of zero potential energy.

For the case of a wave traveling in the direction of decreasing x, the eigenfunction and wave function are

$$\psi(x) = Be^{-ikx} \qquad \text{and} \qquad \Psi(x,t) = Be^{i(-kx-\omega t)} \tag{6-10}$$

When we operate on Ψ with p_{op}, the sign reversal of the kx term in the former leads to a sign reversal in the result. This, in turn, leads to a momentum expectation value of

$$\bar{p} = -\sqrt{2mE}$$

Therefore, we interpret the eigenfunction, and wave function, as describing the motion of a particle which is moving in the direction of decreasing x with negative momentum of the magnitude that would be expected in consideration of its energy.

The eigenfunctions and wave functions just considered represent the *idealized* situations of a particle moving, in one direction or the other, in a beam of infinite length. Its x coordinate is completely unknown because the amplitudes of the waves are the same in all regions of the x axis. That is, the probability densities, for instance

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

are constants independent of x. Thus the particle is equally likely to be found anywhere, and the uncertainty in its position is $\Delta x = \infty$. The uncertainty principle states that in these situations we may know the value of the momentum p of the particle with complete precision, since

$$\Delta p \, \Delta x \geq \hbar/2$$

can be satisfied for an uncertainty in its momentum of $\Delta p = 0$, if $\Delta x = \infty$. Perfectly precise values of p are also indicated by the de Broglie relation, $p = \hbar k$, because these wave functions contain only a single value of the wave number k. Since there is an infinite amount of time available to measure the energy of a particle traveling through a beam of infinite length, the energy-time uncertainty principle $\Delta E \, \Delta t \geq \hbar/2$ allows its energy to be known with complete precision. This agrees with the presence of a single value of the angular frequency ω in these wave functions, because the de Broglie-Einstein relation $E = \hbar\omega$ shows this means a single value of the energy E.

A physical example approximating the idealized situation represented by these wave functions would be a proton moving in a highly monoenergetic beam emerging from a cyclotron. Such beams are used to study the scattering of protons by targets of nuclei inserted in the beam. From the point of view of the target nucleus, and in terms of distances of the order of its nuclear radius r', the x position of a proton in the beam may be for all practical purposes completely unknown. That is $\Delta x \gg r'$. Thus the free particle wave functions of (6-9) and (6-10) can give a good approximation to the description of the beam proton in the region of interest near the nucleus where the scattering takes place. In other words, near a nucleus the wave function of (6-9)

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

can be used to describe a proton in a cyclotron beam directed towards increasing x, providing the beam is extremely long compared to the dimensions of the nucleus—a condition which is always satisfied in practice since nuclei are extremely small. The wave function describes a particle moving with momentum precisely $p = \hbar k$ and total energy precisely $E = \hbar\omega$, where these quantities are related by the equation $p = \sqrt{2mE}$ appropriate to a particle of mass m moving in a region of zero potential energy.

There is a difficulty concerning the normalization of the wave functions of (6-9) and (6-10). In order to have, for instance

$$\int_{-\infty}^{\infty} \Psi^*\Psi \, dx = \int_{-\infty}^{\infty} A^*A \, dx = A^*A \int_{-\infty}^{\infty} dx = 1$$

the amplitude A must be zero as $\int_{-\infty}^{\infty} dx$ has an infinite value. The difficulty arises from the unrealistic statement made by the wave function that the particle can be found with equal probability anywhere in a beam of infinite length. This is never really true since real beams are always of finite length. The proton beam is limited on one end by the cyclotron and on the other end by a laboratory wall. Although the uncertainty Δx in location of a proton is very much larger than a nuclear radius r', it is not larger than the distance L from the cyclotron to the wall. That is, even though $\Delta x \gg r'$, it is also true that $\Delta x < L$. This suggests that normalization can be obtained by setting $\Psi = 0$ outside of the range $-L/2 < x < +L/2$, or else by restricting x to be within that range. In either way we obtain a more realistic description of the actual physical situation, and we can also normalize the wave function with a nonvanishing amplitude A. The procedure is called *box normalization*. Despite the fact that the value of A obtained depends on the length L of the box, it always turns out that the final result of calculation of a measurable quantity is independent of the actual value of L used. Furthermore, we shall see that it is usually not necessary to carry through box normalization in detail because quantities of physical interest can be expressed as ratios in which the value of A cancels.

The situation is quite analogous to ones commonly encountered in classical physics. For instance, in solving a problem of electrostatics, a straight charged wire of infinite length is often used to approximate one of finite length in a system where "end effects" are not important. This idealization very much simplifies the geometry of the problem, but it leads to the difficulty that an infinite amount of energy is required to charge the infinitely long wire, unless its charge density is zero. It is usually possible, however, to get around this difficulty simply by expressing the quantities that arise in the problem in terms of ratios.

It is possible to obtain a much more realistic sense of motion than is seen in either part of Figure 6-1 by using a large number of wave functions of the form of (6-9) to generate a *group* of traveling waves. Figure 6-2 shows the probability density $\Psi^*\Psi$ for a particularly simple group, its motion in the direction of increasing x, and the ever increasing width of the group. At any instant the location of the group can be well characterized by the expectation value $\bar{x}$, calculated from the probability density. The constant velocity of the group, $d\bar{x}/dt$, equals the constant velocity of the free particle, $v = p/m = \sqrt{2mE}/m = \sqrt{2E/m}$, in agreement with the conclusions of Chapter 3. The spreading of the group is a characteristic property of waves that is intimately related to the uncertainty principle, as discussed in that chapter. Of course the behavior of the group wave function is easier to interpret than the behavior of a purely sinusoidal wave function, such as that of (6-9), because the corresponding probability density is closer to the description of particle motion we are familiar with from classical mechanics. However the mathematics required to describe the group, and treat its behavior analytically, is much more complicated. The reason is that a group must necessarily involve a distribution of wave numbers k, and therefore a distribution of energies $E = \hbar^2k^2/2m$. In order to compose even as simple a group as the one shown in the figure, a very large number of sinusoidal waves, with very small differences in wave numbers or energies, must be summed in the manner described in Chapter 3. These mathematical complications far outweigh any advantages involved

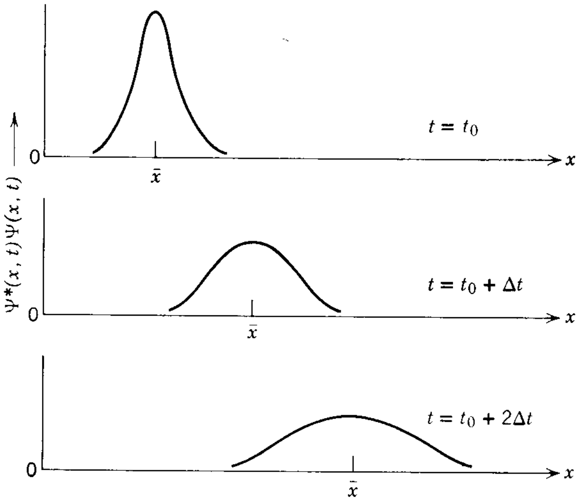

FIGURE 6-2

The probability density $\Psi^*\Psi$ for a group traveling wave function of a free particle. With increasing time the group moves in the direction of increasing x, and also spreads.

in the ease of interpretation. Consequently, groups are rarely used in practical quantum mechanical calculations, and most such calculations are performed with wave functions involving a single wave number and energy.

Our consideration of the motion of the group in Figure 6-2 leads us to discuss briefly a related case of great interest. If, instead of having the constant value zero, the potential function $V(x)$ changes so slowly that its value is almost constant over a distance of the order of the de Broglie wavelength of the particle, the group wave function will still propagate in a manner similar to that illustrated in the figure, but the velocity of the group will now also change slowly. Calculations, starting from the Schroedinger equation, lead to an expression relating the change in the velocity, $d\bar{x}/dt$, of the group to the change in the potential, $V(x)$. The expression is

$$\frac{d}{dt}\left(\frac{d\bar{x}}{dt}\right) = \overline{\frac{d}{dx}\left(-\frac{V(x)}{m}\right)}$$

or

$$\frac{d^2\bar{x}}{dt^2} = \frac{-\overline{\dfrac{dV(x)}{dx}}}{m} = \frac{\overline{F(x)}}{m}$$

where the bars denote expectation values and $F(x)$ is the force corresponding to the potential $V(x)$. It is unfortunate that the calculations are too complicated to reproduce here. They are very significant because they show that the acceleration of the average location of the particle associated with the group wave function equals the average force acting on the particle, divided by its mass. That is, Schroedinger's equation leads to the result that Newton's law of motion is obeyed, on the average, by a particle of a microscopic system. The fluctuations from its average behavior reflect the uncertainty principle, and they are very important in the microscopic limit. But these fluctuations become negligible in the macroscopic limit where the uncertainty principle is of no consequence, and it is no longer necessary to speak of averages in talking about locations in that limit. Also, in the macroscopic limit any realistic potential changes by only a small amount in a distance as short as a de Broglie wavelength. So it is also not necessary, in that limit, to speak of averages when discussing potentials. Thus, in the macroscopic limit we can ignore the bars representing expectation values, or averages, in the equations just displayed. We then conclude that *Newton's law of motion can be derived from the Schroedinger equation, in the classical limit of macroscopic systems. Newton's law of motion is a special case of Schroedinger's equation.*

6-3 The Step Potential (Energy Less Than Step Height)

In the next sections we shall study solutions to the time-independent Schroedinger equation for a particle whose potential energy can be represented by a function $V(x)$ which has a different constant value in each of several adjacent ranges of the x axis. These potentials change in value abruptly in going from one range to the adjacent range. Of course potentials which change abruptly (i.e., are discontinuous functions of x) do not really exist in nature. Nevertheless, these idealized potentials are used frequently in quantum mechanics to approximate real situations because, being constant in each range, they are easy to treat mathematically. The results we obtain for these potentials will allow us to illustrate a number of characteristic quantum mechanical phenomena.

An analogy, that is surely familiar to the student, is found in the procedure used in studying electromagnetism. This involves treating many idealized systems like the infinite wire, the capacitor without edges, etc. These systems are studied because they are relatively easy to handle, because they are excellent approximations to real ones, and because real systems are usually complicated to treat mathematically since they have complicated geometries. The idealized potentials we treat in this chapter are used in the same way and with the same justification.

The simplest case is the *step potential*, illustrated in Figure 6-3. If we choose the origin of the x axis to be at the step, and the arbitrary additive constant that always occurs in the definition of a potential energy so that the potential energy of the particle is zero when it is to the left of the step, $V(x)$ can be written

$$V(x) = \begin{matrix} V_0 & \qquad\qquad x > 0 \\ 0 & \qquad\qquad x < 0 \end{matrix} \tag{6-11}$$

where V_0 is a constant. We may think of $V(x)$ as an approximate representation of the potential energy function for a charged particle moving along the axis of a system of two electrodes, separated by a very narrow gap, which are held at different voltages. The upper half of Figure 6-4 illustrates this system, and the lower half illustrates the corresponding potential energy function. As the gap decreases, the potential function approaches the idealization illustrated in Figure 6-3. In Example 6-2 we shall see that the potential energy for an electron moving near the surface of a metal is very much like a step potential since it rapidly increases at the surface from an essentially constant interior value to a higher constant exterior value.

Assume that a particle of mass m and total energy E is in the region $x < 0$, and that it is moving toward the point $x = 0$ at which the step potential $V(x)$ abruptly changes its value. According to classical mechanics, the particle will move freely in that region until it reaches $x = 0$, where it is subjected to an impulsive force $F = -dV(x)/dx$ acting in the direction of decreasing x. The idealized potential, (6-11), yields an impulsive force of infinite magnitude acting only at the point $x = 0$. However, as it acts on the particle only for an infinitesimal time, the quantity $\int F\,dt$ (the