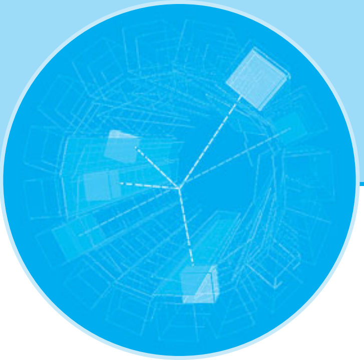
CHAPTER 6



The Schrödinger Equation

The success of the de Broglie relations in predicting the diffraction of electrons and other particles, and the realization that classical standing waves lead to a discrete set of frequencies, prompted a search for a wave theory of electrons analogous to the wave theory of light. In this electron wave theory, classical mechanics should appear as the short-wavelength limit, just as geometric optics is the short-wavelength limit of the wave theory of light. The genesis of the correct theory went something like this, according to Felix Bloch,[1] who was present at the time:

> . . . in one of the next colloquia, Schrödinger gave a beautifully clear account of how de Broglie associated a wave with a particle and how he [i.e., de Broglie] could obtain the quantization rules . . . by demanding that an integer number of waves should be fitted along a stationary orbit. When he had finished Debye[2] casually remarked that he thought this way of talking was rather childish . . . [that to] deal properly with waves, one had to have a wave equation.

In 1926, Erwin Schrödinger[3] published his now-famous wave equation, which governs the propagation of matter waves, including those of electrons. A few months earlier, Werner Heisenberg had published a seemingly different theory to explain atomic phenomena. In the Heisenberg theory, only measurable quantities appear. Dynamical quantities such as energy, position, and momentum are represented by matrices, the diagonal elements of which are the possible results of measurement. Though the Schrödinger and Heisenberg theories appear to be different, it was eventually shown by Schrödinger himself that they were equivalent, in that each could be derived from the other. The resulting theory, now called *wave mechanics* or *quantum mechanics*, has been amazingly successful. Though its principles may seem strange to us, whose experiences are limited to the macroscopic world, and though the mathematics required to solve even the simplest problem is quite involved, there seems to be no alternative to describe correctly the experimental results in atomic and nuclear physics. In this book we will confine our study to the Schrödinger theory because it is easier to learn and is a little less abstract than the Heisenberg theory. We will begin by restricting our discussion to problems in one space dimension.

6-1 The Schrödinger Equation in One Dimension

The wave equation governing the motion of electrons and other particles with mass, which is analogous to the classical wave equation (Equation 5-11), was found by Schrödinger late in 1925 and is now known as the Schrödinger equation. Like the classical wave equation, the Schrödinger equation relates the time and space derivatives of the wave function. The reasoning followed by Schrödinger is somewhat difficult and not important for our purposes. In any case, it must be emphasized that we can't derive the Schrödinger equation just as we can't derive Newton's laws of motion. *Its validity, like that of any fundamental equation, lies in its agreement with experiment.* Just as Newton's second law is not relativistically correct, neither is Schrödinger's equation, which must ultimately yield to a relativistic wave equation. But, as you know, Newton's laws of motion are perfectly satisfactory for solving a vast array of nonrelativistic problems. So, too, will be Schrödinger's equation when applied to the equally extensive range of nonrelativistic problems in atomic, molecular, and solid-state physics. Schrödinger tried without success to develop a relativistic wave equation, a task accomplished in 1928 by Dirac.

Although it would be logical merely to postulate the Schrödinger equation, we can get some idea of what to expect by first considering the wave equation for photons, which is Equation 5-11 with speed $v = c$ and with $y(x, t)$ replaced by the electric field $\mathcal{E}(x, t)$.

$$\frac{\partial^2 \mathcal{E}}{\partial x^2} = \frac{1}{c^2}\frac{\partial^2 \mathcal{E}}{\partial t^2} \qquad \textbf{6-1}$$

As discussed in Chapter 5, a particularly important solution of this equation is the harmonic wave function $\mathcal{E}(x, t) = \mathcal{E}_0 \cos(kx - \omega t)$. Differentiating this function twice, we obtain

$$\frac{\partial^2 \mathcal{E}}{\partial t^2} = -\omega^2 \mathcal{E}_0 \cos(kx - \omega t) = -\omega^2 \mathcal{E}(x, t)$$

and

$$\frac{\partial^2 \mathcal{E}}{\partial x^2} = -k^2 \mathcal{E}(x, t)$$

Substitution into Equation 6-1 then gives

$$-k^2 = -\frac{\omega^2}{c^2}$$

or

$$\omega = kc \qquad \textbf{6-2}$$

Using $\omega = E/\hbar$ and $p = \hbar k$ for electromagnetic radiation, we have

$$E = pc \qquad \textbf{6-3}$$

which, as we saw earlier, is the relation between the energy and momentum of a photon.

Erwin Schrödinger. [*Courtesy of the Niels Bohr Library, American Institute of Physics.*]

Now let us use the de Broglie relations for a particle such as an electron to find the relation between ω and k that is analogous to Equation 6-2 for photons. We can then use this relation to work backward and see how the wave equation for electrons must differ from Equation 6-1. The total energy (nonrelativistic) of a particle of mass m is

$$E = \frac{p^2}{2m} + V \qquad \textbf{6-4}$$

where V is the potential energy. Substituting the de Broglie relations (Equations 5-21 and 5-22) in Equation 6-4, we obtain

$$\hbar\omega = \frac{\hbar^2 k^2}{2m} + V \qquad \textbf{6-5}$$

This differs from Equation 6-2 for a photon because it contains the potential energy V and because the angular frequency ω does not vary linearly with k. Note that we get a factor of ω when we differentiate a harmonic wave function with respect to time and a factor of k when we differentiate with respect to position. We expect, therefore, that the wave equation that applies to electrons will relate the *first* time derivative to the *second* space derivative and will also involve the potential energy of the electron.

Finally, we require that the wave equation for electrons will be a differential equation that is linear in the wave function $\Psi(x, t)$, This ensures that, if $\Psi_1(x, t)$ and $\Psi_2(x, t)$ are both solutions of the wave equation for the same potential energy, then any arbitrary linear combination of these solutions is also a solution—i.e., $\Psi(x, t) = a_1\Psi_1(x, t) + a_2\Psi_2(x, t)$ is a solution, with a_1 and a_2 being arbitrary constants. Such a combination is called *linear* because both $\Psi_1(x, t)$ and $\Psi_2(x, t)$ appear only to the first power. Linearity guarantees that the wave functions will add together to produce constructive and destructive interference, which we have seen to be a characteristic of matter waves, as well as all other wave phenomena. Note, in particular, that (1) the linearity requirement means that *every* term in the wave equation must be linear in $\Psi(x, t)$ and (2) that *any* derivative of $\Psi(x, t)$ is linear in $\Psi(x, t)$.[4]

The Schrödinger Equation

We are now ready to postulate the Schrödinger equation for a particle of mass m. In one dimension, it has the form

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + V(x,t)\Psi(x,t) = i\hbar\frac{\partial\Psi(x,t)}{\partial t} \tag{6-6}$$

We will now show that this equation is satisfied by a harmonic wave function in the special case of a free particle, one on which no net force acts, so that the potential energy is constant, $V(x, t) = V_0$. First note that a function of the form $\cos(kx - \omega t)$ does not satisfy this equation because differentiation with respect to time changes the cosine to a sine, but the second derivative with respect to x gives back a cosine. Similar reasoning rules out the form $\sin(kx - \omega t)$. However, the exponential form of the harmonic wave function does satisfy the equation. Let

$$\begin{aligned}\Psi(x,t) &= Ae^{i(kx-\omega t)} \\ &= A[\cos(kx-\omega t) + i\sin(kx-\omega t)]\end{aligned} \tag{6-7}$$

where A is a constant. Then

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

and

$$\frac{\partial^2\Psi}{\partial x^2} = (ik)^2Ae^{i(kx-\omega t)} = -k^2\Psi$$

Substituting these derivatives into the Schrödinger equation with $V(x, t) = V_0$ gives

$$\frac{-\hbar^2}{2m}(-k^2\Psi) + V_0\Psi = i\hbar(-i\omega)\Psi$$

or

$$\frac{\hbar^2k^2}{2m} + V_0 = \hbar\omega$$

which is Equation 6-5.

An important difference between the Schrödinger equation and the classical wave equation is the explicit appearance[5] of the imaginary number $i = (-1)^{1/2}$. The wave functions that satisfy the Schrödinger equation are not necessarily real, as we see from the case of the free-particle wave function of Equation 6-7. Evidently the wave function $\Psi(x, t)$ which solves the Schrödinger equation is not a directly measurable function as the classical wave function $y(x, t)$ is since measurements always yield real numbers. However, as we discussed in Section 5-4, the probability of finding the electron in dx is certainly measurable, just as is the probability that a flipped coin will turn up heads. The probability $P(x)dx$ that the electron will be found in the volume dx was defined by Equation 5-23 to be equal to $|\Psi|^2\,dx$. This probabilistic interpretation of Ψ was developed by Max Born and was recognized, over the early and formidable objections of both Schrödinger and Einstein, as the appropriate way of relating solutions of the Schrödinger equation to the results of physical measurements. The probability that an electron is in the region dx, a real number, can be measured by counting the fraction of time it is found there in a very large number of identical trials. In recognition of the complex nature of $\Psi(x, t)$, we must modify slightly the interpretation of the wave function discussed in Chapter 5 to accommodate Born's interpretation so that the probability of finding the electron in dx is real. We take for the probability

$$P(x, t)\,dx = \Psi^*(x, t)\Psi(x, t)\,dx = |\Psi(x, t)|^2\,dx \qquad \textbf{6-8}$$

where Ψ^*, the complex conjugate of Ψ, is obtained from Ψ by replacing i with $-i$ wherever it appears.[6] The complex nature of Ψ serves to emphasize the fact that, in reality, we should not ask or try to answer the question, "What is waving in a matter wave?" or inquire as to what medium supports the motion of a matter wave. The wave function is a computational device with utility in Schrödinger's theory of wave mechanics. Physical significance is associated not with Ψ itself, but with the product $\Psi^*\Psi = |\Psi|^2$, which is the probability distribution $P(x, t)$ or, as it is often called, the *probability density*. In keeping with the analogy with classical waves and wave functions, $\Psi(x, t)$ is also sometimes referred to as the *probability density amplitude*, or just the *probability amplitude*.

The probability of finding the electron in dx at x_1 or in dx at x_2 is the sum of separate probabilities, $P(x_1)\,dx + P(x_2)\,dx$. Since the electron must certainly be somewhere in space, the sum of the probabilities over all possible values of x must equal 1. That is[7]

$$\int_{-\infty}^{+\infty} \Psi^*\Psi\,dx = 1 \qquad \textbf{6-9}$$

Equation 6-9 is called the *normalization condition*. This condition plays an important role in quantum mechanics, for it places a restriction on the possible solutions of the Schrödinger equation. In particular, the wave function $\Psi(x, t)$ must approach zero sufficiently fast as $x \rightarrow \pm\infty$ so that the integral in Equation 6-9 remains finite. If it does not, then the probability becomes unbounded. As we will see in Section 6-3, it is this restriction together with boundary conditions imposed at finite values of x that leads to energy quantization for bound particles.

In the chapters that follow, we are going to be concerned with solutions to the Schrödinger equation for a wide range of real physical systems, but in what follows in this chapter, our intent is to illustrate a few of the techniques of solving the equation and to discover the various, often surprising properties of the solutions. To this end we will focus our attention on one-dimensional problems, as noted earlier, and use some potential energy functions with unrealistic physical characteristics, e.g., infinitely rigid walls, which will enable us to illustrate various properties of the solutions without obscuring the discussion with overly complex mathematics.

Separation of the Time and Space Dependencies of $\Psi(x, t)$

Schrödinger's first application of his wave equation was to problems such as the hydrogen atom (Bohr's work) and the simple harmonic oscillator (Planck's work), in which he showed that the energy quantization in those systems can be explained naturally in terms of standing waves. We referred to these in Chapter 4 as stationary states, meaning they did not change with time. Such states are also called *eigenstates*. For such problems that also have potential energy functions that are independent of time, the space and time dependence of the wave function can be separated, leading to a greatly simplified form of the Schrödinger equation.[8] The separation is accomplished by first assuming that $\Psi(x, t)$ can be written as a product of two functions, one of x and one of t, as

$$\Psi(x, t) = \psi(x)\phi(t) \tag{6-10}$$

If Equation 6-10 turns out to be incorrect, we will find that out soon enough, but it turns out that *if* the potential function is *not* an explicit function of time, i.e., if the potential is given by $V(x)$, our assumption turns out to be valid. That this is true can be seen as follows:

Substituting $\Psi(x, t)$ from Equation 6-10 into the general, time-dependent Schrödinger equation (Equation 6-6) yields

$$\frac{-\hbar^2}{2m}\frac{\partial^2\psi(x)\phi(t)}{\partial x^2} + V(x)\psi(x)\phi(t) = i\hbar\frac{\partial\psi(x)\phi(t)}{\partial t} \tag{6-11}$$

which is

$$\frac{-\hbar^2}{2m}\phi(t)\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x)\phi(t) = i\hbar\psi(x)\frac{d\phi(t)}{dt} \tag{6-12}$$

where the derivatives are now ordinary rather than partial ones. Dividing Equation 6-12 by Ψ in the assumed product form $\psi\phi$ gives

$$\frac{-\hbar^2}{2m}\frac{1}{\psi(x)}\frac{d^2\psi(x)}{dx^2} + V(x) = i\hbar\frac{1}{\phi(t)}\frac{d\phi(t)}{dt} \tag{6-13}$$

Notice that each side of Equation 6-13 is a function of only one of the independent variables x and t. This means that, for example, changes in t cannot affect the value of the left side of Equation 6-13, and changes in x cannot affect the right side. Thus, both sides of the equation must be equal to the same constant C, called the *separation constant*, and we see that the assumption of Equation 6-10 is valid—the variables have been separated. We have thus replaced a partial differential equation containing two independent variables, Equation 6-6, with two ordinary differential equations each a function of only one of the independent variables:

$$\frac{-\hbar^2}{2m}\frac{1}{\psi(x)}\frac{d^2\psi(x)}{dx^2} + V(x) = C \tag{6-14}$$

$$i\hbar\frac{1}{\phi(t)}\frac{d\phi(t)}{dt} = C \tag{6-15}$$

Let us solve Equation 6-15 first. The reason for doing so is twofold: (1) Equation 6-15 does not contain the potential $V(x)$; consequently, the time-dependent part $\phi(t)$ of *all* solutions $\Psi(x, t)$ to the Schrödinger equation will have the same form when the potential is not an explicit function of time, so we only have to do this once. (2) The separation constant C has particular significance that we want to discover before we tackle Equation 6-14. Writing Equation 6-15 as

$$\frac{d\phi(t)}{\phi(t)} = \frac{C}{i\hbar}\,dt = -\frac{iC}{\hbar}\,dt \qquad \textbf{6-16}$$

The general solution of Equation 6-16 is

$$\phi(t) = e^{-iCt/\hbar} \qquad \textbf{6-17}\boldsymbol{a}$$

which can also be written as

$$\phi(t) = e^{-iCt/\hbar} = \cos\left(\frac{Ct}{\hbar}\right) - i\sin\left(\frac{Ct}{\hbar}\right) = \cos\left(2\pi\frac{Ct}{h}\right) - i\sin\left(2\pi\frac{Ct}{h}\right) \qquad \textbf{6-17}\boldsymbol{b}$$

Thus, we see that $\phi(t)$, which describes the time variation of $\Psi(x, t)$, is an oscillatory function with frequency $f = C/h$, However, according to the de Broglie relation (Equation 5-1), the frequency of the wave represented by $\Psi(x, t)$ is $f = E/h$; therefore, we conclude that the separation constant $C = E$, the total energy of the particle, and we have

$$\phi(t) = e^{-iEt/\hbar} \qquad \textbf{6-17}\boldsymbol{c}$$

for all solutions to Equation 6-6 involving time-independent potentials. Equation 6-14 then becomes, on multiplication by $\psi(x)$,

$$\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \qquad \textbf{6-18}$$

Equation 6-18 is referred to as the *time-independent Schrödinger equation*.

The time-independent Schrödinger equation in one dimension is an ordinary differential equation in one variable x and is therefore much easier to handle than the general form of Equation 6-6. The normalization condition of Equation 6-9 can be expressed in terms of $\psi(x)$, since the time dependence of the absolute square of the wave function cancels. We have

$$\Psi^*(x, t)\Psi(x, t) = \psi^*(x)e^{+iEt/\hbar}\psi(x)e^{-iEt/\hbar} = \psi^*(x)\psi(x) \qquad \textbf{6-19}$$

and Equation 6-9 then becomes

$$\int_{-\infty}^{+\infty} \psi^*(x)\psi(x)dx = 1 \qquad \textbf{6-20}$$

Conditions for Acceptable Wave Functions

The form of the wave function $\psi(x)$ that satisfies Equation 6-18 depends on the form of the potential energy function $V(x)$. In the next few sections we will study some simple but important problems in which $V(x)$ is specified. Our example potentials will be approximations to real physical potentials, simplified to make calculations easier.

In some cases, the slope of the potential energy may be discontinuous, e.g., $V(x)$ may have one form in one region of space and another form in an adjacent region. (This is a useful mathematical approximation to real situations in which $V(x)$ varies rapidly over a small region of space, such as at the surface boundary of a metal.) The procedure in such cases is to solve the Schrödinger equation separately in each region of space and then require that the solutions join smoothly at the point of discontinuity.

Since the probability of finding a particle cannot vary discontinuously from point to point, the wave function $\psi(x)$ must be continuous.[9] Since the Schrödinger equation involves the second derivative $d^2\psi/dx^2 = \psi''$, the first derivative ψ' (which is the slope) must also be continuous. That is, the graph of $\psi(x)$ versus x must be smooth. (In a special case in which the potential energy becomes infinite, this restriction is relaxed. Since no particle can have infinite potential energy, $\psi(x)$ must be zero in regions where $V(x)$ is infinite. Then, at the boundary of such a region, ψ' may be discontinuous.)

If either $\psi(x)$ or $d\psi/dx$ were not finite or not single valued, the same would be true of $\Psi(x, t)$ and $d\Psi/dx$. As we will shortly see, the predictions of wave mechanics regarding the results of measurements involve both of those quantities and would thus not necessarily predict finite or definite values for real physical quantities. Such results would not be acceptable since measurable quantities, such as angular momentum and position, are never infinite or multiple valued. A final restriction on the form of the wave function $\psi(x)$ is that in order to obey the normalization condition, $\psi(x)$ must approach zero sufficiently fast as $x \to \pm\infty$ so that normalization is preserved. For future reference, we may summarize the conditions that the wave function $\psi(x)$ must meet in order to be acceptable as follows:

1. $\psi(x)$ must exist and satisfy the Schrödinger equation.
2. $\psi(x)$ and $d\psi/dx$ must be continuous.
3. $\psi(x)$ and $d\psi/dx$ must be finite.
4. $\psi(x)$ and $d\psi/dx$ must be single valued.
5. $\psi(x) \to 0$ fast enough as $x \to \pm\infty$ so that the normalization integral, Equation 6-20, remains bounded.

Note that, given Equation 6-10, the acceptability conditions above ultimately apply to $\Psi(x, t)$.

Questions

1. Like the classical wave equation, the Schrödinger equation is linear. Why is this important?
2. There is no factor $i = (-1)^{1/2}$ in Equation 6-18. Does this mean that $\psi(x)$ must be real?
3. Why must the electric field $\mathscr{E}(x, t)$ be real? Is it possible to find a nonreal wave function that satisfies the classical wave equation?
4. Describe how the de Broglie hypothesis enters into the Schrödinger wave equation.
5. What would be the effect on the Schrödinger equation of adding a constant rest energy for a particle with mass to the total energy E in the de Broglie relation $f = E/h$?
6. Describe in words what is meant by normalization of the wave function.

EXAMPLE 6-1 A Solution to the Schrödinger Equation Show that for a free particle of mass m moving in one dimension, the function $\psi(x) = A \sin kx + B \cos kx$ is a solution to the time-independent Schrödinger equation for any values of the constants A and B.

SOLUTION

A free particle has no net force acting upon it, e.g., $V(x) = 0$, in which case the kinetic energy equals the total energy. Thus, $p = \hbar k = (2mE)^{1/2}$. Differentiating $\psi(x)$ gives

$$\frac{d\psi}{dx} = kA \cos kx - kB \sin kx$$

and differentiating again,

$$\begin{aligned}\frac{d^2\psi}{dx^2} &= -k^2 A \sin kx - k^2 B \cos kx \\ &= -k^2(A \sin kx + B \cos kx) = -k^2\psi(x)\end{aligned}$$

Substituting into Equation 6-18,

$$\frac{-\hbar^2}{2m}[(-k^2)(A \sin kx + B \cos kx)] = E(A \sin kx + B \cos kx)$$

$$\frac{\hbar^2 k^2}{2m}\psi(x) = E\psi(x)$$

and, since $\hbar^2 k^2 = 2mE$, we have

$$E\psi(x) = E\psi(x)$$

and the given $\psi(x)$ is a solution of Equation 6-18.

6-2 The Infinite Square Well

A problem that provides several illustrations of the properties of wave functions and is also one of the easiest problems to solve using the time-independent, one-dimensional Schrödinger equation is that of the infinite square well, sometimes called the particle in a box. A macroscopic example is a bead moving on a frictionless wire between two massive stops clamped to the wire. We could also build such a "box" for an electron using electrodes and grids in an evacuated tube, as illustrated in Figure 6-1*a*. The walls of the box are provided by the increasing potential between the grids G and the electrode C as shown in Figures 6-1*b* and *c*. The walls can be made arbitrarily high and steep by increasing the potential V and reducing the separation between each grid-electrode pair. In the limit such a potential energy function looks like that in Figure 6-2, which is a graph of the potential energy of an infinite square well. For this problem the potential energy is of the form

$$\begin{aligned}V(x) &= 0 \qquad 0 < x < L \\ V(x) &= \infty \qquad x < 0 \quad \text{and} \quad x > L\end{aligned} \tag{6-21}$$

Although such a potential is clearly artificial, the problem is worth careful study for several reasons: (1) exact solutions to the Schrödinger equation can be obtained