

Although the direct computational approach is limited to systems with only a few degrees of freedom, the simplicity of this approach will aid our understanding of the behavior of quantum systems. After a summary of the general features of quantum mechanical systems in Section 16.2, we consider this approach to solving the time-independent Schrödinger equation in Sections 16.3 and 16.4. In Section 16.5, we use a half-step algorithm to generate wave packet solutions to the time-dependent Schrödinger equation.

Because we have already learned that the diffusion equation (16.1) can be formulated as a random walk problem, it might not surprise you that Schrödinger's equation can be analyzed in a similar way. Monte Carlo methods are introduced in Section 16.7 to obtain variational solutions of the ground state. We introduce quantum Monte Carlo methods in Section 16.8 and discuss more sophisticated quantum Monte Carlo methods in Sections 16.9 and 16.10.

## 16.2 ■ REVIEW OF QUANTUM THEORY

For simplicity, we consider a one-dimensional, nonrelativistic quantum system consisting of one particle. The state of the system is completely characterized by the position space wave function  $\Psi(x, t)$ , which is interpreted as a probability amplitude. The probability  $P(x, t) \Delta x$  of the particle being in a "volume" element  $\Delta x$  centered about the position  $x$  at time  $t$  is equal to

$$P(x, t) \Delta x = |\Psi(x, t)|^2 \Delta x, \quad (16.2)$$

where  $|\Psi(x, t)|^2 = \Psi(x, t)\Psi^*(x, t)$ , and  $\Psi^*(x, t)$  is the complex conjugate of  $\Psi(x, t)$ . This interpretation of  $\Psi(x, t)$  requires the use of normalized wave functions such that

$$\int_{-\infty}^{\infty} \Psi^*(x, t) \Psi(x, t) dx = 1. \quad (16.3)$$

If the particle is subjected to the influence of a potential energy function  $V(x, t)$ , the evolution of  $\Psi(x, t)$  is given by the time-dependent Schrödinger equation

$$i\hbar \frac{\partial \Psi(x, t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} + V(x, t) \Psi(x, t), \quad (16.4)$$

where  $m$  is the mass of the particle, and  $\hbar$  is Planck's constant divided by  $2\pi$ .

Physically measurable quantities, such as the momentum, have corresponding operators. The expectation or average value of an observable  $A$  is given by

$$\langle A \rangle = \int \Psi^*(x, t) \hat{A} \Psi(x, t) dx, \quad (16.5)$$

where  $\hat{A}$  is the operator corresponding to the measurable quantity  $A$ . For example, the momentum operator corresponding to the linear momentum  $p$  is  $\hat{p} = -i\hbar \partial / \partial x$  in position space.

If the potential energy function is independent of time, we can obtain solutions of (16.4) of the form

$$\Psi(x, t) = \phi(x) e^{-iEt/\hbar}. \quad (16.6)$$

A particle in the state (16.6) has a well-defined energy  $E$ . If we substitute (16.6) into (16.4), we obtain the time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m} \frac{d^2 \phi(x)}{dx^2} + V(x) \phi(x) = E \phi(x). \quad (16.7)$$

Note that  $\phi(x)$  is an *eigenstate* of the Hamiltonian operator

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x), \quad (16.8)$$

with the *eigenvalue*  $E$ . That is,

$$\hat{H} \phi(x) = E \phi(x). \quad (16.9)$$

In general, there are many eigenstates  $\phi_n$ , each with eigenvalue  $E_n$ , that satisfy (16.9) and the boundary conditions imposed on the eigenstates by physical considerations.

The general form of  $\Psi(x, t)$  can be expressed as a superposition of the eigenstates of the operator corresponding to any physical observable. For example, if  $\hat{H}$  is independent of time, we can write

$$\Psi(x, t) = \sum_n c_n \phi_n(x) e^{-iE_n t/\hbar}, \quad (16.10)$$

where  $\Sigma$  represents a sum over the discrete states and an integral over the continuum states. The coefficients  $c_n$  in (16.10) can be determined from the value of  $\Psi(x, t)$  at any time  $t$ . For example, if we know  $\Psi(x, t = 0)$ , we can use the orthonormality property of the eigenstates of any physical operator to obtain

$$c_n = \int \phi_n^*(x) \Psi(x, 0) dx. \quad (16.11)$$

The coefficient  $c_n$  can be interpreted as the probability amplitude of a measurement of the total energy yielding a particular value  $E_n$ .

There are three steps needed to solve (16.7) numerically. The first is to integrate (16.7) for any given value of the energy  $E$  in a way similar to the approach we have used for numerically solving other ordinary differential equations. This approach will usually not satisfy the boundary conditions. The second step is to find the particular values of  $E$  that lead to solutions that satisfy the boundary conditions. Finally, we need to normalize the eigenstate wave function using (16.3) so that we can interpret the eigenstate as a probability amplitude.

We first discuss the solution of (16.7) without imposing any boundary conditions by treating the solution to (16.7) as an initial value problem for the wave function and its derivative at some value of  $x$  for a given value of  $E$ . We will use these solutions to develop our intuition about the behavior of one-dimensional solutions to the Schrödinger equation.