In momentum space the kinetic energy operator is equivalent to multiplying by the kinetic energy $p^2/2m$. The middle term in (16.50) operates by multiplying points on the momentum grid by a phase factor that is proportional to the kinetic energy:

$$\tilde{\Phi}_j = e^{-ip_j^2 \Delta t/2m} \Phi_j. \tag{16.52}$$

The split-operator algorithm jumps back and forth between position and momentum space to propagate the wave function. The algorithm starts in position space where each grid value $\Psi_j = \Psi(x_j, t)$ is multiplied by (16.51). The wave function is then transformed to momentum space where every momentum value $\Phi_j$ is multiplied by (16.52). It is then transformed back to position space where (16.51) is applied a second time. A single time step can therefore be written as

$$\Psi(x, t + \Delta t) = e^{-iV(x)\Delta t/2\hbar} F^{-1}\left[e^{-ip^2 \Delta t/2m} F[e^{-iV(x)\Delta t/2\hbar}\Psi(x, t)]\right], \tag{16.53}$$

where $F$ is the Fourier transform to momentum space and $F^{-1}$ is its inverse.

**Problem 16.22 Split-operator algorithm**

(a) Write a program to implement the split-operator algorithm. It is necessary to evaluate the exponential phase factors only once when implementing the split-operator algorithm. Store the complex exponentials in arrays that match the $x$-values on the spatial grid and the $p$-values on the momentum grid. Use wrap-around order when storing the momentum phase factors because the `FFT` class inverse transformation assumes that data are in wrap-around order. You can use the `getWrappedOmega` method in the FFT to obtain the momenta in this ordering.

(b) Compare the evolution of a Gaussian wave packet using the split-operator and half-step algorithms using identical grids. How does the finite grid size affect each algorithm?

(c) Compare the computation speed of the split-operator and half-step algorithms using a Gaussian wave packet in a square well. Disable plotting and other nonessential computations when comparing the speeds. ■

**Problem 16.23 Split-operator accuracy**

The split-operator and half-step algorithms fail if the time step is too large. Use both algorithms to evolve a simple harmonic oscillator coherent state (see Problem 16.14). Describe the error that occurs if the time step becomes too large. ■

## 16.7 ■ VARIATIONAL METHODS

One way of obtaining a good approximation of the ground state energy is to use a variational method. This approach has numerous applications in chemistry, atomic and molecular physics, nuclear physics, and condensed matter physics. Consider a system whose Hamiltonian operator $\hat{H}$ is given by (16.8). According to the variational principle, the expectation value of the Hamiltonian for an arbitrary trial wave function $\Psi$ is greater than or equal to



the ground state energy $E_0$. That is,

$$\langle H \rangle = E[\Psi] = \frac{\int \Psi^*(x)\hat{H}\Psi(x)\,dx}{\int \Psi^*(x)\Psi(x)\,dx} \geq E_0, \tag{16.54}$$

where $E_0$ is the exact ground state energy of the system. We assume that the wave function is continuous and bounded. The inequality (16.54) reduces to an equality only if $\Psi$ is an eigenstate of $\hat{H}$ with the eigenvalue $E_0$. For bound states, $\Psi$ may be assumed to be real without loss of generality so that $\Psi^* = \Psi$ and thus $|\Psi(x)|^2 = \Psi(x)^2$. This assumption implies that we do not need to store two values representing the real and imaginary parts of $\Psi$.

The inequality (16.54) is the basis of the variational method. The procedure is to choose a physically reasonable form for the trial wave function $\Psi(x)$ that depends on one or more parameters. The expectation value $E[\Psi]$ is computed, and the parameters are varied until a minimum of $E[\Psi]$ is obtained. This value of $E[\Psi]$ is an upper bound to the true ground state energy. Often forms of $\Psi$ are chosen so that the integrals in (16.54) can be done analytically. To avoid this restriction we can use numerical integration methods.

In most applications of the variational method, the integrals in (16.54) are multidimensional and Monte Carlo integration methods are essential. For this reason we will use Monte Carlo integration in the following, even though we will consider only one- and two-body problems. Because it is inefficient to simply choose points at random to compute $E[\Psi]$, we rewrite (16.54) in a form that allows us to use importance sampling. We write

$$E[\Psi] = \frac{\int \Psi(x)^2 E_L(x)\,dx}{\int \Psi(x)^2\,dx}, \tag{16.55}$$

where $E_L$ is the *local energy*

$$E_L(x) = \frac{\hat{H}\Psi(x)}{\Psi(x)}, \tag{16.56}$$

which can be calculated analytically using the trial wave function. The form of (16.55) is that of a weighted average with the weight equal to the normalized probability density $\Psi(x)^2/\int \Psi(x)^2\,dx$. As discussed in Section 11.6, we can sample values of $x$ using the distribution $\Psi(x)^2$ so that the Monte Carlo estimate of $E[\Psi]$ is given by the sum

$$E[\Psi] = \lim_{n\to\infty} \frac{1}{n} \sum_{i=1}^{n} E_L(x_i), \tag{16.57}$$

where $n$ is the number of times that $x$ is sampled from $\Psi^2$. How can we sample from $\Psi^2$? In general, it is not possible to use the inverse transform method (see Section 11.5) to generate a nonuniform distribution. A convenient alternative is the Metropolis method which has the advantage that only an unnormalized $\Psi^2$ is needed for the proposed move.

**Problem 16.24 Ground state energy of several one-dimensional systems**

(a) It is useful to test the variational method on an exactly solvable problem. Consider the one-dimensional harmonic oscillator with $V(x) = x^2/2$. Choose the trial wave