

function to be $\Psi(x) \propto e^{-\lambda x^2}$, with λ the variational parameter. Generate values of x chosen from a normalized $\Psi^2(x)$ using the inverse transform method and verify that $\lambda = 1/2$ yields the smallest upper bound by considering $\lambda = 1/2$ and four other values of λ near $1/2$. Another way to generate a Gaussian distribution is to use the Box-Muller method discussed in Section 11.5.

- (b) Repeat part (a) using the Metropolis method to generate x distributed according to $\Psi(x)^2 \propto e^{-2\lambda x^2}$ and evaluate (16.57). As discussed in Section 11.7, the Metropolis method can be summarized by the following steps:

- Choose a trial position $x_{\text{trial}} = x_n + \delta_n$, where δ_n is a uniform random number in the interval $[-\delta, \delta]$.
- Compute $w = p(x_{\text{trial}})/p(x_n)$, where in this case $p(x) = e^{-2\lambda x^2}$.
- If $w \geq 1$, accept the change and let $x_{n+1} = x_{\text{trial}}$.
- If $w < 1$, generate a random number r and let $x_{n+1} = x_{\text{trial}}$ if $r \leq w$.
- If the trial change is not accepted, then let $x_{n+1} = x_n$.

Remember that it is necessary to wait for equilibrium (convergence to the distribution Ψ^2) before computing the average value of E_L . Look for a systematic trend in $\langle E_L \rangle$ over the course of the random walk. Choose a step size δ that gives a reasonable value for the acceptance ratio. How many trials are necessary to obtain $\langle E_L \rangle$ to within 1% accuracy compared to the exact analytic result?

- (c) Instead of finding the minimum of $\langle E_L \rangle$ as a function of the various variational parameters, minimize the quantity

$$\sigma_L^2 = \langle E_L^2 \rangle - \langle E_L \rangle^2. \quad (16.58)$$

Verify that the exact minimum value of $\sigma_L^2[\Psi]$ is zero, whereas the exact minimum value of $E_L[\Psi]$ is unknown in general.

- Consider the anharmonic potential $V(x) = \frac{1}{2}x^2 + bx^4$. Plot $V(x)$ as a function of x for $b = 1/8$. Use first-order perturbation theory to calculate the lowest order change in the ground state energy due to the x^4 term. Then choose a reasonable form for your trial wave function and use your Monte Carlo program to estimate the ground state energy. How does your result compare with first-order perturbation theory?
- Consider the anharmonic potential of part (d) with $b = -1/8$. Plot $V(x)$. Use first-order perturbation theory to calculate the lowest order change in the ground state energy due to the x^4 term and then use your program to estimate E_0 . Do your Monte Carlo estimates for the ground state energy have a lower bound? Why or why not?
- Modify your program so that it can be applied to the ground state of the hydrogen atom. In this case we have $V(r) = -e^2/r$, where e is the magnitude of the charge on the electron. The element of integration dx in (16.55) is replaced by $4\pi r^2 dr$. Choose $\Psi \propto e^{-r/a}$, where a is the variational parameter. Measure lengths in terms of the Bohr radius \hbar^2/me^2 and energy in terms of the Rydberg $me^4/2\hbar^2$. In these units $\mu = e^2 = \hbar = 1$. Find the optimal value of a . What is the corresponding energy?
- Consider the Yukawa or screened Coulomb potential for which $V(r) = -e^2 e^{-\alpha r}/r$, where $\alpha > 0$. In this case the ground state and wave function can only be obtained numerically. For $\alpha = 0.5$ and $\alpha = 1.0$ the most accurate numerical estimates of E_0 are -0.14808 and -0.01016 , respectively. What is a good choice for the form of the trial wave function? How close can you come to these estimates? ■

Problem 16.25 Variational estimate of the ground state of Helium

Helium has long served as a testing ground for atomic trial wave functions. Consider the ground state of the helium atom with the interaction

$$V(r_1, r_2) = -2e^2 \left(\frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{e^2}{r_{12}}, \quad (16.59)$$

where r_{12} is the separation between the two electrons. Assume that the nucleus is fixed and ignore relativistic effects. Choose $\Psi(\mathbf{r}_1, \mathbf{r}_2) = Ae^{-Z_{\text{eff}}(r_1+r_2)/a_0}$, where Z_{eff} is a variational parameter. Estimate the upper bound to the ground state energy based on this functional form of Ψ . ■

Our discussion of variational Monte Carlo methods has been only introductory in nature. One important application of variational Monte Carlo methods is to optimize a given trial wave function which is then used to “guide” the Monte Carlo methods discussed in Sections 16.8 and 16.9.

16.8 ■ RANDOM WALK SOLUTIONS OF THE SCHRÖDINGER EQUATION

We now introduce a Monte Carlo approach based on expressing the Schrödinger equation in imaginary time. This approach follows that of Anderson (see references). We will then discuss several other *quantum Monte Carlo* methods. We will see that although the systems of interest are quantum mechanical, we can convert them to systems for which we can use classical Monte Carlo methods.

To understand how we can interpret the Schrödinger equation in terms of a random walk in imaginary time, we substitute $\tau = it/\hbar$ into the time-dependent Schrödinger equation for a free particle and write (in one dimension)

$$\frac{\partial \Psi(x, \tau)}{\partial \tau} = \frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, \tau)}{\partial x^2}. \quad (16.60)$$

Note that (16.60) is identical in form to the diffusion equation (16.1). Hence, we can interpret the wave function Ψ as a probability density with a diffusion constant $D = \hbar^2/2m$.

From our discussion in Chapter 7, we know that we can use the formal similarity between the diffusion equation and the imaginary-time free particle Schrödinger equation to solve the latter by replacing it by an equivalent random walk problem. To understand how we can interpret the role of the potential energy term in the context of random walks, we write Schrödinger's equation in imaginary time as

$$\frac{\partial \Psi(x, \tau)}{\partial \tau} = \frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, \tau)}{\partial x^2} - V(x)\Psi(x, \tau). \quad (16.61)$$

If we were to ignore the first term (the diffusion term) on the right side of (16.61), the result would be a first-order differential equation corresponding to a decay or growth process depending on the sign of V . We can obtain the solution to this first-order equation by replacing it by a random decay or growth process, for example, radioactive decay. These considerations suggest that we can interpret (16.61) as a combination of diffusion and branching processes. In the latter, the number of walkers increases or decreases at a point x depending