where

$$F(x) = \frac{2}{\Psi_T}\frac{\partial \Psi_T}{\partial x}, \tag{16.87}$$

and the local energy $E_L(x)$ is given by

$$E_L(x) = \frac{\hat{H}\Psi_T}{\Psi_T} = V(x) - \frac{D}{\Psi_T}\frac{\partial^2 \Psi_T}{\partial x^2}. \tag{16.88}$$

The term in (16.86) containing F corresponds to a drift in the walkers away from regions where $|\Psi_T|^2$ is small (see Problem 7.43).

To incorporate the drift term into $G_{\text{diffusion}}$, we replace $(x - x')^2$ in (16.82) by the term $(x - x' - D\Delta\tau F(x'))^2$ so that the diffusion propagator becomes

$$G_{\text{diffusion}}(x, x', \Delta\tau) = (4\pi D\Delta\tau)^{-1/2} e^{-(x-x'-D\Delta\tau F(x'))^2/4D\Delta\tau}. \tag{16.89}$$

However, this replacement destroys the symmetry between x and x'. To restore it, we use the Metropolis algorithm for accepting the new position of a walker. The acceptance probability p is given by

$$p = \frac{|\Psi_T(x')|^2\, G_{\text{diffusion}}(x, x', \Delta\tau)}{|\Psi_T(x)|^2\, G_{\text{diffusion}}(x', x, \Delta\tau)}. \tag{16.90}$$

If $p > 1$, we accept the move; otherwise, we accept the move if $r \leq p$. The branching step is achieved by using (16.83) with $V(x) + V(x')$ replaced by $E_L(x) + E_L(x')$ and $\Delta\tau$ replaced by an effective time step. The reason for the use of an effective time step in (16.83) is that some diffusion steps are rejected. The effective time step to be used in (16.83) is found by multiplying $\Delta\tau$ by the average acceptance probability. It can be shown (see Hammond et al.) that the mean value of the local energy is an unbiased estimator of the ground state energy.

Another possible improvement is to periodically replace branching (which changes the number of walkers) with a weighting of the walkers. At each weighting step, each walker is weighted by G_{branch}, and the total number of walkers remains constant. After n steps, the kth walker receives a weight $W_k = \Pi_{i=1}^{n} G_{\text{branch}}^{(i,k)}$, where $G_{\text{branch}}^{(i,k)}$ is the branching factor of the kth walker at the ith time step. The contribution to any average quantity of the kth walker is weighted by W_k.

Problem 16.29 Diffusion quantum Monte Carlo

(a) Modify `QMWalkApp` to implement the diffusion quantum Monte Carlo method for the system considered in Problem 16.26 or 16.27. Begin with $N_0 = 100$ walkers and $\Delta\tau = 0.01$. Use at least three values of $\Delta\tau$ and extrapolate your results to $\Delta\tau \to 0$. Reasonable results can be obtained by adjusting the reference energy every 20 Monte Carlo steps with $a = 0.1$.

(b) Write a program to apply the diffusion quantum Monte Carlo method to the hydrogen atom. In this case a configuration is represented by three coordinates.

*(c) Modify your program to include weights in addition to changing walker populations. Redo part (a) and compare your results. ■

***Problem 16.30 Importance sampling**

(a) Derive the partial differential equation (16.86) for $f(x, \tau)$.

(b) Modify `QMWalkApp` to implement the diffusion quantum Monte Carlo method with importance sampling. Consider the harmonic oscillator problem with the trial wave function $\Psi_T = e^{-\lambda x^2}$. Compute the statistical error associated with the ground state energy as a function of λ. How much variance reduction can you achieve relative to the naive diffusion quantum Monte Carlo method? Then consider another form of Ψ_T that does not have a form identical to the exact ground state. Try the hydrogen atom with $\Psi_T = e^{-\lambda r}$. ■

16.10 ■ PATH INTEGRAL QUANTUM MONTE CARLO

The Monte Carlo methods we have discussed so far are primarily useful for estimating the ground state energy and wave function, although it is also possible to find the first few excited states with some effort. In this section we discuss a Monte Carlo method that is of particular interest for computing the thermal properties of quantum systems.

We recall (see Section 7.10) that classical mechanics can be formulated in terms of the principle of least action. That is, given two points in space-time, a classical particle chooses the path that minimizes the action given by

$$S = \int_{x_0,0}^{x,t} L\, dt. \tag{16.91}$$

The Lagrangian L is given by $L = T - V$. Quantum mechanics also can be formulated in terms of the action (cf. Feynman and Hibbs). The result of this *path integral* formalism is that the real-time propagator G can be expressed as

$$G(x, x_0; t) = A \sum_{\text{paths}} e^{iS/\hbar}, \tag{16.92}$$

where A is a normalization factor. The sum in (16.92) is over all paths between $(x_0, 0)$ and (x, t), not just the path that minimizes the classical action. The presence of the imaginary number i in (16.92) leads to interference effects. As before, the propagator $G(x, x_0, t)$ can be interpreted as the probability amplitude for a particle to be at x at time t given that it was at x_0 at time zero. G satisfies the equation (see (16.75))

$$\Psi(x, t) = \int G(x, x_0, t)\Psi(x_0, 0)\, dx_0 \quad (t > 0). \tag{16.93}$$

Because G satisfies the same differential equation as Ψ in both x and x_0, G can be expressed as

$$G(x, x_0, t) = \sum_n \phi_n(x)\phi_n(x_0)e^{-iE_n t/\hbar}, \tag{16.94}$$