$(H - V_{\text{ref}})$, we can verify that G satisfies the equation

$$\frac{\partial G}{\partial \tau} = -(\hat{H} - V_{\text{ref}})G, \tag{16.76}$$

which is the same form as the imaginary-time Schrödinger equation (16.65). It is easy to verify that $G(x, x', \tau) = G(x', x, \tau)$. A formal solution of (16.76) is

$$G(\tau) = e^{-(\hat{H} - V_{\text{ref}})\tau}, \tag{16.77}$$

where the meaning of the exponential of an operator is given by its Taylor series expansion.

The difficulty with (16.77) is that the kinetic and potential energy operators $\hat{T}$ and $\hat{V}$ in $\hat{H}$ do not commute. For this reason, if we want to write the exponential in (16.77) as a product of two exponentials, we can only approximate the exponential for short times $\Delta\tau$. To first order in $\Delta\tau$ (higher-order terms involve the commutator of $\hat{V}$ and $\hat{H}$), we have

$$G(\Delta\tau) \approx G_{\text{branch}} G_{\text{diffusion}} \tag{16.78}$$

$$= e^{-(V - V_{\text{ref}})\Delta\tau} e^{-\hat{T}\Delta\tau}, \tag{16.79}$$

where $G_{\text{diffusion}} \equiv e^{-\hat{T}\Delta\tau}$ and $G_{\text{branch}} \equiv e^{-(\hat{V} - V_{\text{ref}})\Delta\tau}$ correspond to the two random processes: diffusion and branching. From (16.76) we see that $G_{\text{diffusion}}$ and G_{branch} satisfy the differential equations

$$\frac{\partial G_{\text{diffusion}}}{\partial \tau} = -\hat{T} G_{\text{diffusion}} = \frac{\hbar^2}{2m} \frac{\partial^2 G_{\text{diffusion}}}{\partial x^2} \tag{16.80}$$

$$\frac{\partial G_{\text{branch}}}{\partial \tau} = (V_{\text{ref}} - \hat{V}) G_{\text{branch}}. \tag{16.81}$$

The solutions to (16.79)–(16.81) that are symmetric in x and x' are

$$G_{\text{diffusion}}(x, x', \Delta\tau) = (4\pi D \Delta\tau)^{-1/2} e^{-(x - x')^2/4D}, \tag{16.82}$$

with $D \equiv \hbar^2/2m$, and

$$G_{\text{branch}}(x, x', \Delta\tau) = e^{-(\frac{1}{2}[V(x) + V(x')] - V_{\text{ref}})\Delta\tau}. \tag{16.83}$$

From the form of (16.82) and (16.83), we can see that the diffusion quantum Monte Carlo method is similar to the random walk algorithm discussed in Section 16.8. An implementation of the diffusion quantum Monte Carlo method in one dimension can be summarized as follows:

1. Begin with a set of N_0 random walkers. There is no lattice, so the positions of the walkers are continuous. It is advantageous to choose the walkers so that they are in regions of space where the wave function is known to be large.
2. Choose one of the walkers and displace it from x to x'. The new position is chosen from a Gaussian distribution with a variance $2D\Delta\tau$ and zero mean. This change corresponds to the diffusion process given by (16.82).

3. Weight the configuration x' by

$$w(x \to x', \Delta\tau) = e^{-(\frac{1}{2}[V(x) + V(x')] - V_{\text{ref}})\Delta\tau}. \tag{16.84}$$

One way to do this weighting is to generate duplicate random walkers at x'. For example, if $w \approx 2$, we would have two walkers at x' where previously there had been one. To implement this weighting (branching) correctly, we must make an integer number of copies that is equal on the average to the number w. A simple way to do so is to take the integer part of $w + r$, where r is a uniform random number in the unit interval. The number of copies can be any nonnegative integer including zero. The latter value corresponds to a removal of a walker.

4. Repeat steps 2 and 3 for all members of the ensemble, thereby creating a new ensemble at a later time $\Delta\tau$. One iteration of the ensemble is equivalent to performing the integration

$$\Psi(x, \tau) = \int G(x, x', \Delta\tau)\, \Psi(x', \tau - \Delta\tau)\, dx'. \tag{16.85}$$

5. The quantity of interest $\Psi(x, \tau)$ will be independent of the original ensemble $\Psi(x, 0)$ if a sufficient number of Monte Carlo steps are taken. As before, we must ensure that $N(\tau)$, the number of walkers at time τ, is kept close to the desired number N_0.

Now we can understand how the simple random walk algorithm discussed in Section 16.8 is an approximation to the diffusion quantum MC algorithm. First, the Gaussian distribution gives the exact distribution for the displacement of a random walker in a time $\Delta\tau$, in contrast to the fixed step size in the simple random walk algorithm which gives the average displacement of a walker. Hence, there are no systematic errors due to the finite step size. Second, if we expand the exponential in (16.83) to first order in $\Delta\tau$ and set $V(x) = V(x')$, we obtain the branching rule used previously. (We use the fact that the uniform distribution r is the same as the distribution $1 - r$.) However, the diffusion quantum MC algorithm is not exact because the branching is independent of the position reached by diffusion, which is only true in the limit $\Delta\tau \to 0$. This limitation is remedied in the Green's function Monte Carlo method where a short time approximation is not made (see the articles on Green's function Monte Carlo in the references).

One limitation of the two random walk methods we have discussed is that they can become very inefficient. This inefficiency is due in part to the branching process. If the potential becomes large and negative (as it is for the Coulomb potential when an electron approaches a nucleus), the number of copies of a walker will become very large. It is possible to improve the efficiency of these algorithms by introducing an importance sampling method. The idea is to use an initial guess $\Psi_T(x)$ for the wave function to guide the walkers toward the more important regions of $V(x)$. To implement this idea, we introduce the function $f(x, \tau) = \Psi(x, \tau)\Psi_T(x)$. If we calculate the quantity $\partial f/\partial t - D\,\partial^2 f/\partial x^2$ and use (16.65), we can show that $f(x, \tau)$ satisfies the differential equation

$$\frac{\partial f}{\partial \tau} = D\frac{\partial^2 f}{\partial x^2} - D\frac{\partial [f F(x)]}{\partial x} - [E_L(x) - V_{\text{ref}}]f, \tag{16.86}$$