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in the derivation of Eq. (4) we can demonstrate that

$$\left(T^\dagger + \frac{\partial}{\partial \tau}\right)g(\mathbf{R}) = \int \left(T^\dagger + \frac{\partial}{\partial \tau}\right)G(\mathbf{R},\mathbf{R}';\tau)g(\mathbf{R}')d\,\mathbf{R}'$$
$$= O(\tau), \qquad (15)$$

where g is an arbitrary function. Here we expand $G_R(\mathbf{R},\mathbf{R}')$ and $g(\mathbf{R}')$ in a Taylor's series about $\mathbf{R}$, and for the integral over $\mathbf{R}'$ we use the fact that this variable has the same moments as $\mathbf{R}$ [Eqs. (12) and (13)].

Equations (4) and (15) provide only a very limited tool in the analysis of the time step error in a Green's function. As an alternative, we recommend the operator approach, which is described shortly. One of us[3] has applied this approach to derive a DMC Green's function with an error of $O(\tau^2)$. Applications of this and similar Green's functions to the ground states of H_2 and LiH have been published by us.[4]

Using the operator approach, one has to simply verify that

$$\lim_{\tau \to 0} \int \left(\frac{\partial}{\partial \tau}\right)G(\mathbf{R},\mathbf{R}';\tau)g(\mathbf{R})d\,\mathbf{R} = T'g(\mathbf{R}'). \qquad (16)$$

For Green's function (1), this is achieved after the following steps: (i) Substitute $G = G_0 G_R$ [Eqs. (9) and (10)], (ii) use the identity

$$\frac{-\partial G_0}{\partial \tau} = -(1/2)\nabla^2 G_0, \qquad (17)$$

(iii) apply Green's theorem, and (iv) take the $\tau \to 0$ limit [where G_0 becomes equal to $\delta(\mathbf{R}' - \mathbf{R})$].

The operator approach also provides the easiest way of constructing the actual simulation algorithm. One applies $\exp(-\tau T^\dagger)$ to a Fourier transform of $\delta(\mathbf{R} - \mathbf{R}')$, which gives directly the *moments* of the random variable $\mathbf{R}'$. Details will be published shortly by one of us.[5]

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[1] J. W. Moskowitz and K. E. Schmidt, J. Chem. Phys. **85**, 2868 (1986).
[2] J. B. Anderson, J. Chem. Phys. **63**, 1499 (1975); **65**, 4121 (1976); **73**, 3897 (1980); P. J. Reynolds, D. M. Ceperley, B. J. Alder, and W. A. Lester, Jr., *ibid.* **77**, 5593 (1982).
[3] J. Vrbik, J. Phys. A **18**, 1327 (1985).
[4] J. Vrbik and S. M. Rothstein, J. Comput. Phys. **63**, 130 (1986); S. M. Rothstein, N. Patil, and J. Vrbik, J. Comput. Chem. (to be published).
[5] J. Vrbik, J. Phys. A (to be published).

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A "short-time approximation" has been used in a number of random walk solutions of the Schrödinger equation. In the appendix to a recent paper,[1] Moscowitz and Schmidt claim to demonstrate that the short-time approximation is incorrect even in the limit of the time step going to zero. They further claim in Ref. 1 that all results[2] obtained with the short-time approximation are incorrect even in the limit of time step going to zero. These claims are wrong. The short-time approximation is correct in the limit of time step going to zero.

In the following paragraphs we first show that the algorithm associated with the approximation leads to an exact simulation of the Schrödinger equation as $\Delta t \to 0$. Then we indicate the errors in logic in Ref. 1, which result from considering a *sufficient* criterion of validity to be a *necessary* criterion.

The random walk method of solving the Schrödinger equation is based on the similarity of the Schrödinger equation in imaginary time $\tau = it$ and the diffusion equation with an added first-order reaction term:

$$-i\hbar \frac{\partial \psi}{\partial t} = \frac{\hbar^2}{2m} \nabla^2 \psi - (V - E_{ref})\psi, \qquad (1)$$

$$\frac{\partial C}{\partial t} = D\nabla^2 C - kC. \qquad (2)$$

In these the usual symbols take their usual meanings, E_{ref} is a reference energy, and the potential energy V and the rate constant k may vary with position R. For use of importance sampling[3] Eq. (1) is multiplied by an approximate wave function ψ_0 and restated in terms of the function $\phi = \psi\psi_0$ which is the product of the exact and approximate wave functions. The resulting equation[4] and the diffusion equation with reaction and drift are isomorphic:

$$-i\hbar \frac{\partial \phi}{\partial t} = \frac{\hbar^2}{2m} \nabla^2 \phi - \nabla \cdot (\phi \nabla \ln|\psi_0|) - (E_{loc} - E_{ref})\phi, \qquad (3)$$

$$\frac{\partial C}{\partial t} = D\nabla^2 C - \nabla \cdot (Cv) - kC. \qquad (4)$$

In these, $\nabla \ln|\psi_0|$ corresponds to the fluid velocity v and $E_{loc} = H\psi_0/\psi_0$ is the local energy.

The algorithm used in simulating Eqs. (1) and (3) is a simple one based on a random walk of particles for the diffusion term with additional steps for the drift term and multiplications and/or disappearances for the reaction term. Since the diffusion equation and the similar heat equation are more often used in the literature of mathematics and since its terms have direct physical meanings, we use Eq. (4) to illustrate the algorithm. According to the algorithm each particle in the system is moved in the time interval Δt from its position at R' to a new position at R selected at random from a Gaussian distribution with variance $2D\Delta t$ centered

on a point at $R' + v(R')\Delta t$. At the new position the particle is replaced by n particles where n is the integer part of $m = \{\exp[-k(R')\Delta t] + u\}$ and u is a random number in the interval $(0,1)$. Additional details are given in Ref. 2.

The change in concentration with time at position R is given (for three dimensions) by

$$\frac{\partial C(R)}{\partial t} = -\frac{C(R)}{\Delta t} + \left(\frac{1}{4\pi D\Delta t}\right)^{3/2}$$

$$\times \int_{-\infty}^{\infty} \exp\left\{\frac{[R'-R-v(R')\Delta t]^2}{4D\Delta t}\right.$$

$$\left. - k(R')\Delta t\right\}\frac{C(R')}{\Delta t}\, dR'. \tag{5}$$

The first term on the right represents the loss of particles from R to all R' and the second represents the gain to R from all R'.

To find the behavior as $\Delta t \to 0$ we expand the variables k, C, and v in the Taylor series about the point R, separate the exponential term into parts and expand the parts in series, drop terms which may be neglected as $\Delta t \to 0$, substitute the remaining expressions for k, C, and v in Eq. (5), carry out the integration, and consider the result.

In carrying out the integration we observe that terms containing odd powers of $(x'-x)$ yield zero and terms containing even powers of $(x'-x)$ greater than the second yield zero in the limit of small time steps. The result is

$$\frac{\partial C}{\partial t} = D\nabla^2 C - \nabla \cdot (Cv) - kC, \tag{6}$$

which is identical to Eq. (4). We conclude that our algorithm gives the correct concentration distribution in the limit as $\Delta t \to 0$.

Although terminology varies somewhat we may consider the algorithm described above to correspond to the Green's function for Eq. (4) in the limit $\Delta t \to 0$. Thus, we have

$$G(R,R',\Delta t)$$

$$= \left(\frac{1}{4\pi D\Delta t}\right)^{3/2}\exp\left\{-\frac{[R'-R-v(R')\Delta t]^2}{4D\Delta t}\right.$$

$$\left. - k(R')\Delta t\right\}, \tag{7}$$

$$C(R,t+\Delta t) = \int G(R,R',\Delta t)C(R',t)dR'. \tag{8}$$

With use of Green's theorem[5] it has been shown[6] that for $k(R) = 0$ and $v(R) = 0$ the Green's function of Eq. (7) is an exact Green's function for Eq. (4) for any Δt (provided that G and C obey the same boundary conditions). If $k(R)$ and $v(R)$ are both constant throughout space, a transformation[7] of coordinates may be used to reduce the problem to that with $k(R) = 0$ and $v(R) = 0$. For these cases G obeys (∇^2 and ∇ in the R system)

$$\frac{\partial G}{\partial t} = D\nabla^2 G - \nabla \cdot (Gv) - kG \quad (\text{const } v,k), \tag{9}$$

and Eq. (9) may be used to prove Eq. (8) is correct. Thus, satisfying Eq. (9) is *sufficient* to show that the Green's function of Eq. (7) is exact for these cases.

The Green's function of Eq. (7) with $k = 0$ and variable v is that tested in Ref. 1 against the criterion of Eq. (9) with $k = 0$ and variable v. It does not satisfy Eq. (9) and although it may be sufficient that it satisfy Eq. (9), it is *not necessary* that it satisfy Eq. (9) in order to be valid. Our analysis above shows that it does satisfy Eq. (4) for $\Delta t \to 0$, and satisfying Eq. (4) is the ultimate criterion.

Some insight into the "sufficient" criterion of Eq. (9) may by gained from examination of Eq. (8) in the manner of Ref. 1. We obtain somewhat different expressions, the differences possibly due to typographical errors in Eqs. (A4) to (A7) of Ref. 1. [We use the R and R' conventions of Eq. (8).]

Substituting our expressions for $\nabla \ln G$ and so forth into a modified Eq. (9) with $k(R') = 0$, the equivalent of Eq. (A3) of Ref. 1, we obtain

$$\sum_{i=1}^{3}\frac{\partial v_i}{\partial x_i}\left[\frac{(x_i'-x_i)^2}{2D\Delta t} - 1\right]$$

$$+ \sum_{i=1}^{3}\sum_{\substack{j=1\\j\neq i}}^{3}\frac{\partial v_i}{\partial x_j}\frac{(x_i'-x_i)(x_j'-x_j)}{2D\Delta t} + O[(\Delta t)^{1/2}] \neq 0. \tag{10}$$

We note that an integration over the R' space in the limit of $\Delta t \to 0$ gives zero for the first term [since the average value of $(x_i'-x_i)^2$ is $2D\Delta t$], zero for the second term [since the average value of $(x_i'-x_i)$ is zero], and zero for the third term. Thus, the integral form of Eq. (9) is satisfied by our G as $\Delta t \to 0$.

In summary, we conclude that in the limit of $\Delta t \to 0$ the short-time algorithm of random walk calculations is correct, the corresponding Green's function is correct, and the results obtained with proper use of them are also correct.

We note that several alternative algortithms[8] giving errors of order $(\Delta t)^2$ are available. These too are correct in the limit of $\Delta t \to 0$.

[1] J. W. Moscowitz and K. E. Schmidt, J. Chem. Phys. 85, 2868 (1986).
[2] J. B. Anderson, J. Chem. Phys. 63, 1499 (1975); 65, 4121 (1976); 73, 3897 (1980); F. Mentch and J. B. Anderson, ibid. 74, 6307 (1981); P. J. Reynolds, D. M. Ceperley, B. J. Alder, and W. A. Lester, Jr., ibid. 77, 5593 (1982). Also, many others.
[3] R. C. Grimm and R. G. Storer, J. Comput. Phys. 7, 134 (1971); M. H. Kalos, D. Levesque, and L. Verlet, Phys. Rev. A 9, 2178 (1974).
[4] D. M. Ceperley (private communication, 1979); D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. 45, 566 (1980); J. B. Anderson, J. Chem. Phys. 73, 3897 (1980).
[5] G. Green, in Mathematical Papers of the Late George Green, edited by N. M. Ferrers (Macmillan, London, 1871), p. 23.
[6] For example, H. S. Carslaw and J. C. Jaeger, Conduction of Heat in Solids (Oxford University, London, 1947), pp. 291–294.
[7] I. Stakgold, Green's Functions and Boundary Value Problems (Wiley, New York, 1979), pp. 183 and 498.
[8] J. Vrbik, J. Phys. A 18, 1327 (1985); J. Vrbik and S. M. Rothstein, J. Comput. Phys. 63, 130 (1986); J. B. Anderson, J. Chem. Phys. 82, 2662 (1985).