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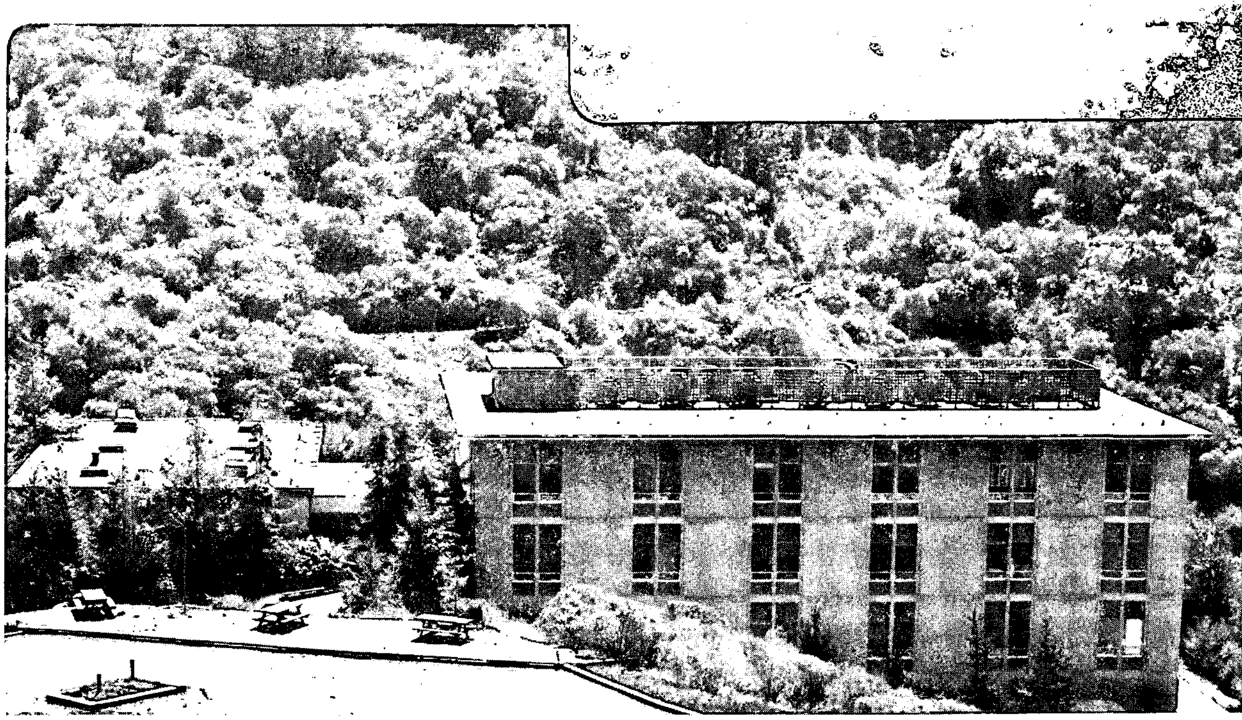

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Is There a Zeroth Order Time-Step Error in Diffusion Quantum Monte Carlo?*

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Abstract.

It is demonstrated that the short-time Green's function often used in diffusion quantum Monte Carlo simulations of the Schrödinger equation generates an unbiased probability distribution in the limit of vanishing time-step, τ. For finite τ, an error is introduced into the potential which is of $O(\tau)$. An expression for this term is derived.

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During the past decade, quantum Monte Carlo methods have been increasingly applied to the determination of the electronic structure of atoms and molecules.[1–6] These Monte Carlo methods are variants of the Green's function Monte Carlo approach of Kalos.[7] Recently, Moskowitz and Schmidt[5] (MS) claim to have proven that the "diffusion" Monte Carlo variant, with a particular choice of short-time Green's function, has a bias which does not vanish as the time step τ approaches zero. In other words, they claim that the short-time Green's function used by a number of workers in the past[2,3] is, in fact, not a correct short-time approximation. In this note we show that their proof is in error, and we derive the correct expression for the short-time bias to order τ.

The Green's function

$$G(\mathbf{R}\rightarrow\mathbf{R}',\tau)=(4\pi D\tau)^{-3N/2}\exp[-\tau\{(E_L(\mathbf{R})+E_L(\mathbf{R}'))/2-E_T\}]$$
$$\times\exp[-\{\mathbf{R}'-\mathbf{R}-D\tau\mathbf{F}(\mathbf{R})\}^2/4D\tau] \qquad (1)$$

used in Refs. 2 and 3, is intended as a propagator for the modified Schrödinger equation

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$$\frac{\partial f}{\partial t}=D\nabla^2 f+[E_T-E_L(\mathbf{R})]f-D\nabla\cdot[f\mathbf{F}(\mathbf{R})] \ , \tag{2}$$

where $E_L(\mathbf{R})$ and $\mathbf{F}(\mathbf{R})$ are known functions,[2-4] $\mathbf{R}$ is the 3N-dimensional vector of the electronic coordinates, and ∇ is the 3N-dimensional extension of the usual gradient operator. Thus,

$$f(\mathbf{R}',t+\tau)=\int d\mathbf{R}\, f(\mathbf{R},t)G(\mathbf{R}\rightarrow\mathbf{R}',\tau) \ . \tag{3}$$

The exact Green's function is a solution to (2) in the variables $\mathbf{R}'$ and τ. Defining the operator L as

$$L\equiv D\nabla^2+[E_T-E_L(\mathbf{R})]-D\nabla\cdot\mathbf{F}-D\mathbf{F}\cdot\nabla-\frac{\partial}{\partial t} \tag{4}$$

and $\hat{L}$ similarly in the variables $\mathbf{R}'$ and τ, one obtains

$$Lf(\mathbf{R},t)=0 \ , \tag{5}$$

and, for the exact G,

$$\hat{L}G^{exact}(\mathbf{R}\rightarrow\mathbf{R}',\tau)=0 \ . \tag{6}$$

As can be seen from substituting Eq. (3) into (2),

$$\hat{L}f(\mathbf{R}',t+\tau)=\int d\mathbf{R}\, f(\mathbf{R},t)\hat{L}G(\mathbf{R}\rightarrow\mathbf{R}',\tau) \ ,$$

and thus using the exact Green's function, $\hat{L}f(\mathbf{R}',t+\tau)=0$, as it should be. On the other hand, for an approximate G such as Eq. (1), there will be remainder terms

$$\hat{L}G=h(\mathbf{R},\mathbf{R}')G \ . \tag{7}$$

Since we are concerned with the asymptotic form of $f(\mathbf{R}',t+\tau)$, we consider the remainder terms that result from $\hat{L}f(\mathbf{R}')$, namely

$$\hat{L}f(\mathbf{R}',t+\tau)=\int d\mathbf{R}\, f(\mathbf{R},t)h(\mathbf{R},\mathbf{R}')G\equiv V'(\mathbf{R}')f(\mathbf{R}',t+\tau) \ . \tag{8}$$

Thus, $(\hat{L}-V')f(\mathbf{R}',t+\tau)=0$. The Schrödinger equation with a modified potential—i.e. Eq. (2) with an additional term $V'f$—is being solved by using the approximate Green's function G. For Eq. (1) to be a correct short-time Green's function $V'(\mathbf{R}')$ must be order τ^{λ}, with $\lambda>0$. MS[5] claim, however, that the error in G is of order τ^0, and is thus of the same order as the potential. To simplify matters, they assume an exact trial wave function, for which $E_L(\mathbf{R})=E_T$=constant. MS then obtain the following expression for $h(\mathbf{R},\mathbf{R}')$ to order τ^0:

$$(2\tau)^{-1}(\mathbf{R}'-\mathbf{R})\cdot[\nabla\{(\mathbf{R}'-\mathbf{R})\cdot\mathbf{F}(\mathbf{R})\}+\mathbf{F}(\mathbf{R})]=(2\tau)^{-1}\sum_{i,j=1}^{3N}(x_i'-x_i)(x_j'-x_j)\frac{\partial F_j}{\partial x_i}\,. \quad (9)$$

The first point to note is that (9) (after integration—i.e. the resulting V') is not only of the same order in τ as V, but is actually of the *same order of magnitude*.[8] This would imply an error in the Monte Carlo energies roughly comparable to the energy itself, independent of τ. In fact, the observed errors are generally less than 0.01% of the total energy, making expression (9) suspect at the outset.

In our analysis, we will make the same assumption MS make about the trial wave function. However, the more general case is not significantly more difficult to analyze, and leads to the same conclusion. With the exact wave function we obtain

$$h(\mathbf{R},\mathbf{R}')=(2\tau)^{-1}[\mathbf{F}(\mathbf{R}')-\mathbf{F}(\mathbf{R})]\cdot[\mathbf{R}'-\mathbf{R}-D\tau\mathbf{F}(\mathbf{R})]-D\nabla'\cdot\mathbf{F}(\mathbf{R}')\,. \quad (10)$$

The $O(\tau^0)$ and $O(\tau^{1/2})$ terms in this expression vanish on average, leaving to lowest order an $O(\tau)$ contribution. This is consistent with observed time-step bias reported in the literature,[3,9] as well as with other theoretical arguments.[10,11] The expression obtained by MS[5] appears to have arisen by their having differentiated with respect to the wrong variable ($\mathbf{R}$ rather than $\mathbf{R}'$).

In order to determine the effect of (10) on the potential, we need to carry out the integration of h (cf. Eq. 8) to obtain V'. In the integral, $\mathbf{F}(\mathbf{R})$ (occurring both in h and in G) and $f(\mathbf{R},t)$ must be Taylor expanded about $\mathbf{R}'$. For ease in performing the Gaussian integrals, these are re-expanded in the variable $\Delta=\mathbf{R}-\mathbf{R}'+D\tau\mathbf{F}(\mathbf{R}')$. We write the expansion for component F_l,

$$F_l(\mathbf{R})=F_l(\mathbf{R}') + \sum_i \frac{\partial F_l}{\partial x_i'}\Big|_{\mathbf{R}'}\Delta_i - D\tau\sum_i \frac{\partial F_l}{\partial x_i'}\Big|_{\mathbf{R}'}F_i(\mathbf{R}')$$
$$+\frac{1}{2}\sum_{ij}\frac{\partial^2 F_l}{\partial x_i'\partial x_j'}\Big|_{\mathbf{R}'}\Delta_i\Delta_j - \frac{D\tau}{2}\sum_{ij}\frac{\partial^2 F_l}{\partial x_i'\partial x_j'}\Big|_{\mathbf{R}'}[\Delta_i F_j(\mathbf{R}')+\Delta_j F_i(\mathbf{R}')]$$
$$+\frac{1}{6}\sum_{ijk}\frac{\partial^3 F_l}{\partial x_i'\partial x_j'\partial x_k'}\Big|_{\mathbf{R}'}\Delta_i\Delta_j\Delta_k + O(\tau^2)\,. \tag{11}$$

Clearly, to $O(\tau^0)$, the term $(2\tau)^{-1}[\mathbf{F}(\mathbf{R}')-\mathbf{F}(\mathbf{R})]\cdot[\mathbf{R}'-\mathbf{R}-D\tau\mathbf{F}(\mathbf{R})]$ in Eq. (10) becomes $(2\tau)^{-1}\sum_{ij}\frac{\partial F_j}{\partial x_i'}\Big|_{\mathbf{R}'}\Delta_i\Delta_j$, whose Gaussian integral becomes $D\nabla\cdot\mathbf{F}(\mathbf{R}')$. Thus to $O(\tau^0)$ $V'(\mathbf{R}')=0$. To $O(\tau^{1/2})$, all integrals are odd, and also vanish. Finally, to $O(\tau)$, we obtain for the error in the potential

$$V'=\tau D^2\left\{\sum_{ij}\left[\left(\frac{\partial F_j}{\partial x_i'}\Big|_{\mathbf{R}'}\right)^2+2F_i(\mathbf{R}')\frac{\partial^2 F_i}{\partial x_j'^2}\Big|_{\mathbf{R}'}+F_i(\mathbf{R}')F_j(\mathbf{R}')\frac{\partial F_j}{\partial x_i'}\Big|_{\mathbf{R}'}+\frac{\partial^3 F_i}{\partial x_i'\partial x_j'^2}\Big|_{\mathbf{R}'}\right]\right\}$$

$$=\tau D^2\left\{\tfrac{1}{2}\nabla^2 F^2+(\mathbf{F}\cdot\nabla)(\nabla\cdot\mathbf{F})+\tfrac{1}{2}\mathbf{F}\cdot\nabla F^2+\nabla^2(\nabla\cdot\mathbf{F})\right\}_{\mathbf{R}=\mathbf{R}'}\,. \tag{12}$$

It is readily argued[12] based on perturbation theory that inclusion of V' in the Schrödinger equation results in an $O(\tau)$ modification to the asymptotic eigenfunction $f(\mathbf{R}')$, and an $O(\tau)$ correction to the energy eigenvalue.

Though this demonstrates that Eq. (1) is a correct short-time Green's function, it has been noted[3,4,11] that this Green's function may fail at the nuclei. This results from the failure of the Taylor expansion of $\mathbf{F}(\mathbf{R})$ at these points. However, the resulting error in the eigenvalues is again[11,12] $O(\tau)$.

In conclusion, we wish to point out that the above discussion rests on the form (1) of the Green's function. In actual usage, other short-time Green's functions are often used.[4,11] Even with Eq. (1), the implementation of the Green's function often contains an additional part:[2–4,13] a rejection step to maintain detailed balance, and/or a deletion or rejection[14] on node crossing to maintain antisymmetry. These terms modify the short-time error obtained in the above analysis. An additional time-step error arises due to the unaccounted node crossing and recrossing which can occur in the course of a single time step. We are at present performing an analysis of the full time-step error within the diffusion quantum Monte Carlo approach. We have thus far found no evidence for a bias which remains in the limit $\tau \rightarrow 0$.

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[8] For example, for the hydrogen atom with a trial wave function of $\Psi_T = e^{-\varsigma r}$, Eq. 9 predicts $V' = \frac{1}{2}\nabla \cdot F = 2\varsigma V$. This would mean that for the exact wave function one has a "perturbation" twice the size of the Coulomb potential.

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