

V. Chester, Phys. Rev. A 10, 303 (1974).

⁵R. N. Barnett, P. J. Reynolds, and W. A. Lester, Jr., J. Comp. Phys. (submitted); preprint.

⁶A. L. L. East, S. M. Rothstein, and J. Vrbik, J. Chem. Phys. 89, 4880 (1988).

⁷M. H. Kalos, D. Levesque, and L. Verlet, Phys. Rev. A 9, 2178 (1974).

⁸Reference 2 gives the most commonly used form correct to $O(t)$. Other

Green's functions provide accuracy to $O(t^2)$, as in S. M. Rothstein, N. Patil, and J. Vrbik, J. Comp. Chem. 8, 412 (1987). Exact Green's function Monte Carlo methods are also available. See, e.g., D. M. Ceperley and M. H. Kalos, in *Monte Carlo Methods in Statistical Physics*, edited by K. Binder (Springer, Berlin, 1979); and D. M. Ceperley and B. J. Alder, J. Chem. Phys. 81, 5833 (1984). We use Eq. (3b) here only for its simplicity in the ensuing arguments.

Reply to "Comment on: 'Sampling the exact electron distribution by diffusion quantum Monte Carlo'"

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In our paper¹ we suggested a simple procedure based on squaring the DQMC weights for estimating the "exact" expectation value of nondifferential quantities. We presented the corresponding sampling as having no error of its own, aside from the fixed-node approximation. However, as Reynolds² has shown in the preceding Comment, our assertion is in error: The procedure will not sample the exact distribution, ϕ^2 .

Nevertheless, recent calculations^{1,3} by us show that our simulated (W^2) distribution provides a very accurate approximation to such sampling. This can be understood from the following perturbation theory argument.

Consider the Schrödinger equations for the variational and DQMC sampling:

$$-\frac{1}{2}\nabla^2 f_1 + \nabla\left(\frac{\nabla\psi}{\psi} f_1\right) = 0, \quad (1)$$

$$-\frac{1}{2}\nabla^2 f_2 + \nabla\left(\frac{\nabla\psi}{\psi} f_2\right) + \left(-\frac{1}{2}\frac{\nabla^2\psi}{\psi} + V - E_0\right)f_2 = 0, \quad (2)$$

respectively. It is the $(E_L - E_0)$ operator which converts the variational distribution $f_1(\psi^2)$ to the mixed one, $f_2(\phi\psi)$. By definition, we consider this operator to be ϵ small, relative to the other terms in Eq. (2).

Now consider the Schrödinger equations for W^2 sampling and for exact ϕ^2 sampling:

$$-\frac{1}{2}\nabla^2 f_3 + \nabla\left(\frac{\nabla\psi}{\psi} f_3\right) + 2\left(-\frac{1}{2}\frac{\nabla^2\psi}{\psi} + V - E_0^{\text{pert}}\right)f_3 = 0, \quad (3)$$

$$-\frac{1}{2}\nabla^2 f_4 + \nabla\left(\frac{\nabla\psi}{\psi} f_4\right) + 2\left(-\frac{1}{2}\frac{\nabla^2\psi}{\psi} + V - E_0\right)f_4 + \left(\frac{\nabla\phi}{\phi} - \frac{\nabla\psi}{\psi}\right)^2 f_4 = 0, \quad (4)$$

respectively. Here f_3 represents our approximation to the exact distribution, due to the absence of the last operator in

Eq. (4). (The corresponding perturbation of E_0 , which unlike f_3 does not result in any improvement over the variational estimate, is not of significance for our argument. The variational energy is already correct to second order in a smallness parameter.)

The error in W^2 sampling arises from the last operator which appears in Eq. (4), but not in Eq. (3). The absence of this operator is now seen to be an ϵ^2 perturbation to the "exact" Eq. (4) as follows:

$(E_L - E_0)$ being ϵ small implies also $(\nabla^2\psi/\psi - \nabla^2\phi/\phi)$ being ϵ small. Now,

$$\nabla\left(\frac{\nabla\phi}{\phi} - \frac{\nabla\psi}{\psi}\right) = -\left(\frac{\nabla\phi}{\phi} - \frac{\nabla\psi}{\psi}\right)\left(\frac{\nabla\phi}{\phi} + \frac{\nabla\psi}{\psi}\right) - \left(\frac{\nabla^2\psi}{\psi} - \frac{\nabla^2\phi}{\phi}\right)$$

or

$$\nabla\mathbf{A} = -\mathbf{A}\cdot\mathbf{B} + \mathbf{C}, \quad (5)$$

where \mathbf{B} is not necessarily small, but \mathbf{C} is ϵ small. This implies that \mathbf{A} is also an operator which is ϵ small in the same sense as $(E_L - E_0)$ is. Then, of course, the "missing" operator, \mathbf{A}^2 is ϵ^2 small.

Further work is necessary to analytically quantify the error introduced by the W^2 sampling scheme.

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¹A. L. L. East, S. M. Rothstein, and J. Vrbik, J. Chem. Phys. 89, 4880 (1988).

²P. J. Reynolds, J. Chem. Phys. 92, 2118 (1990).

³J. Vrbik, D. A. Legare, and S. M. Rothstein, J. Chem. Phys. 92, 1221 (1990).