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Quantum Chemistry by Quantum Monte Carlo: Beyond Ground-State Energy Calculations*

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Abstract.

We present recent advances with the quantum Monte Carlo (QMC) method in its application to molecular systems. The QMC method is a procedure for solving the Schrödinger equation statistically, by the simulation of an appropriate random process. The formal similarity of the Schrödinger equation with a diffusion equation allows one to calculate quantum mechanical expectation values as Monte Carlo averages over an ensemble of random walks. We have previously obtained highly accurate correlation energies for a number of molecules, as well as the singlet-triplet splitting in methylene and the barrier height for the $H + H_2$ exchange reaction. Recently we have begun a program of extending the QMC approach to the calculation of analytic derivatives of the energy. A brief description of the approach is presented here, together with some preliminary results. In addition, we are now computing expectation values of properties other than the energy. We summarize how standard QMC must be modified, and present some results for H_2 and N_2. Finally, we describe preliminary work toward the goal of obtaining accurate molecular excited states through QMC.

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I. Introduction

In the past few years, quantum mechanical Monte Carlo (QMC) methods have begun to make a contribution to quantum chemistry [1-4]. The Monte Carlo technique is complementary to traditional *ab initio* approaches for obtaining molecular properties. The principle behind the two techniques is, however, quite different. In particular, QMC uses the formal similarity of the Schrödinger equation to a diffusion equation to solve the former statistically [1].

Until now, however, QMC applications have been limited to calculations of energies of ground-states and lowest states of a given symmetry. Using QMC, workers have studied molecular correlation energies [1,2] as well as critical points on potential-energy surfaces [3]. A calculation of the singlet-triplet splitting in methylene has also been carried out [4]. The two states studied, however, are both lowest-energy states of their respective symmetries. In these studies, the accuracies obtained with QMC have been comparable to the best achieved by other rigorous methods. Here we discuss our recent effort in extending QMC to molecular properties other than the energy (Sect. II), to energy derivatives (Sect. III), and to excited states of the same symmetry as the ground state (Sect. IV). Preliminary results of this work are presented.

II. QMC Molecular Properties

The QMC method of obtaining energies has been described in detail elsewhere [1-5]. The key point to note here is that a simulation is performed in which an ensemble of random walks (the coordinates of which, at any given time, represent a "configuration" of the electrons) evolve to an equilibrium distribution. At any time after equilibrium has been reached, the ensemble of configurations is a random sample drawn from the probability distribution $f_{\infty}(\underline{R})=\Psi_T(\underline{R})\hat{\phi}(\underline{R})$. Here $\Psi_T(\underline{R})$ is a simple trial wave function used for importance sampling [1,5,6], and in the present applications also for determining the nodes of the problem (i.e. the nodes of Ψ_T are imposed on $\hat{\phi}$) [1,7]; the coordinate vector $\underline{R}$ is the multi-dimensional vector describing the full many-body system. The function $\hat{\phi}(\underline{R})$ is the lowest-energy eigenfunction of the Schrödinger equation for the imposed set of nodes. Although neither this function nor f_∞ is known analytically, we can nevertheless sample desired quantities from the equilibrium distribution. Averages taken with respect to the distribution f_∞ are known as mixed averages. For example, sampling a quantity A in equilibrium after N samples gives the average (in the limit of large N)

$$\begin{aligned} \frac{1}{N}\sum_{configs} A &= <A>_{f_\infty} \\ &\equiv \int f_\infty(\underline{R})\, A \; d\underline{R} \qquad (1) \\ &= \frac{\int \Psi_T(\underline{R})\hat{\phi}(\underline{R})\, A \; d\underline{R}}{\int \Psi_T(\underline{R})\hat{\phi}(\underline{R})\; d\underline{R}} \,, \end{aligned}$$

or in abbreviated Dirac notation (with the normalization absorbed),

$$<A>_{f_\infty} = <\Psi_T \mid A \mid \hat{\phi}> . \qquad (2)$$

On the other hand, the correct expectation value of A, for an eigenstate $\hat{\phi}$, is $<\hat{\phi} \mid A \mid \hat{\phi}>$. In computing the energy, or any property for which $\hat{\phi}$ is an eigenstate, there is no difference between these two averages. This follows since the eigenvalue can be taken out of the integral in the numerator of Eq. 1. In particular, to compute the energy one samples the quantity $E_L(\underline{R}) = \Psi_T^{-1}(\underline{R}) H \Psi_T(\underline{R})$. Then

$$\begin{aligned} <E> &= \frac{\int \hat{\phi}(\underline{R})\Psi_T(\underline{R})[\Psi_T^{-1}(\underline{R}) H \Psi_T(\underline{R})]\; d\underline{R}}{\int \hat{\phi}(\underline{R})\Psi_T(\underline{R})\; d\underline{R}} \\ &= <\hat{\phi} \mid H \mid \Psi_T> = \hat{E}_0 \,, \qquad (3) \end{aligned}$$

where $\hat{E}_0$ is the eigenvalue corresponding to the state $\hat{\phi}$. The last equality follows upon noting that H is Hermitian, and thus can operate to the left.

For expectation values of quantities whose operators do not commute with H, the mixed average is only approximate. One suspects that the mixed average is in some sense "half-way" between the exact expectation value (with respect to $\hat{\phi}$) and the variational expectation value, taken with respect to the trial wave function, i.e. $<\Psi_T \mid A \mid \Psi_T>$. Taken literally, this implies that $<\hat{\phi} \mid A \mid \hat{\phi}> = 2<\Psi_T \mid A \mid \hat{\phi}> - <\Psi_T \mid A \mid \Psi_T>$. This result can be formalized through the following argument. The trial function Ψ_T, if it is good, differs from $\hat{\phi}$ only by a "small" function Δ, i.e. $\hat{\phi}=\Psi_T+\Delta$. Then (see also [5b])

$$\begin{aligned} <\hat{\phi} \mid A \mid \hat{\phi}> &= <\Psi_T \mid A \mid \hat{\phi}> + <\Delta \mid A \mid \hat{\phi}> \\ &\approx <\Psi_T \mid A \mid \hat{\phi}> + <\Delta \mid A \mid \Psi_T> \\ &= 2<\Psi_T \mid A \mid \hat{\phi}> - <\Psi_T \mid A \mid \Psi_T> . \end{aligned} \tag{4}$$

The first equality follows on expanding the $\hat{\phi}$ bra. The approximation in the next line occurs on expanding the $\hat{\phi}$ ket in the second term, and dropping the resulting term of order Δ^2. Finally, Δ is re-expanded; A is assumed an observable, and hence Hermitian. This gives an approximate formula for expectation values taken solely with respect to $\hat{\phi}$ from just mixed and variational averages. The above argument ignores the different normalizations implicit in the different terms. However, it is easy to demonstrate that Eq. 4 divided by $<\hat{\phi} \mid \hat{\phi}>$ differs from $2<\Psi_T \mid A \mid \hat{\phi}>/<\Psi_T \mid \hat{\phi}> - <\Psi_T \mid A \mid \Psi_T>/<\Psi_T \mid \Psi_T>$ by terms of only $O(\Delta^2)$. This gives the desired result. It is, however, difficult to know how significant it is to drop terms of order Δ^2. Thus, it is desirable to be able to sample exactly from the distribution $\mid \hat{\phi} \mid ^2$. This can be done [8], though with some changes to the usual QMC algorithm. The distribution f_∞ must be weighted locally by $\hat{\phi}(\underline{R})/\Psi_T(\underline{R})$. This quantity is essentially the asymptotic number of survivors of the local configuration $\underline{R}$ [8]. Thus, algorithmically, one must follow each configuration into the future before computing any averages. Details of our algorithm will be presented elsewhere [9]. Our results (see Tables 1 and 2) show that while the variational approximation is poor, the approximate formula (Eq. 4) is quite good. Furthermore, excellent agreement with exact results is obtained by sampling from the pure $|\hat{\phi}|^2$ distribution.

III. Energy Derivatives

While conventional *ab initio* approaches regularly compute the analytic derivative of the energy with respect to nuclear coordinates in order to determine equilibrium geometries [10] and (by finite difference or higher analytic derivatives) vibrational frequencies [11], only finite difference approaches have been implemented in QMC [12]. In principle there is no reason for this limitation. To compute the energy derivative with respect to a nuclear coordinate ρ, we write

$$\frac{d<E>_{f_\infty}}{d\rho}=\frac{d}{d\rho}\left\{\frac{\int\hat{\phi}(\underline{R})\Psi_T(\underline{R})\,E_L(\underline{R})\,d\underline{R}}{\int\hat{\phi}(\underline{R})\Psi_T(\underline{R})\,d\underline{R}}\right\}$$

$$=<\frac{\partial E_L}{\partial\rho}>_{f_\infty}$$

$$+<\frac{1}{\hat{\phi}}\frac{\partial\hat{\phi}}{\partial\rho}E_L>_{f_\infty}-<\frac{1}{\hat{\phi}}\frac{\partial\hat{\phi}}{\partial\rho}>_{f_\infty}<E_L>_{f_\infty}$$

$$+<\frac{1}{\Psi_T}\frac{\partial\Psi_T}{\partial\rho}E_L>_{f_\infty}-<\frac{1}{\Psi_T}\frac{\partial\Psi_T}{\partial\rho}>_{f_\infty}<E_L>_{f_\infty}. \qquad (5)$$

The second equality is obtained from differentiation using the chain rule, followed by expression of the resulting ratios as averages over the distribution f_∞. The derivative $\partial\hat{\phi}/\partial\rho$ is unknown; it is however possible to sample it. The other terms in Eq. 5 may be evaluated straight-forwardly during the QMC simulation. Rather than sampling $\partial\hat{\phi}/\partial\rho$, as a first approximation we may take $\hat{\phi}^{-1}\partial\hat{\phi}/\partial\rho=\Psi_T^{-1}\partial\Psi_T/\partial\rho$. This turns out to be a good approximation even when Ψ_T is only of moderate accuracy (e.g. double-zeta Hartree-Fock).

Using this approach, we have performed calculations on H_2 at a few nuclear separations. Our results are presented in Table 3, where they are compared with the essentially exact work of Kolos and Wolniewicz [13], as well as with the results of conventional *ab initio* approaches. As can be seen, QMC is competitive with CI, and far superior to Hartree-Fock at the equilibrium geometry. Studies are in progress at other nuclear geometries, and on other molecular systems.

IV. Excited States

Work thus far with QMC has been limited to ground-state potential-energy surfaces and lowest energy states of a particular symmetry [1-4]. This restriction comes from an essential feature of the mapping of the Schrödinger equation into its diffusion analog--that time in these two equations differs by a factor of i. This means that the expansion of a time-dependent molecular state vector in energy eigenfunctions multiplied by $\exp(-iEt/\hbar)$, results in a series in which only the lowest energy term (i.e. $\hat{\phi}$) survives at large t. Thus one obtains exponential convergence to the lowest energy eigenstate.

If Ψ_T is orthogonal to the exact lowest-energy state, one can see from Eq. 3 that convergence will be to the next-lowest energy. (Initially $\hat{\phi}$ contains a superposition of states.) This fact allows the calculation of molecular energies to begin with, as Fermi energies are excited states (with respect to the Boson ground state) of the Schrödinger equation. By choosing Ψ_T to be antisymmetric with respect to particle exchange, one projects out all symmetric states. A similar result holds for calculations of different symmetry states of a given molecule.

When studying states of the same symmetry, it is generally not possible to find a trial wave function exactly orthogonal to all the lower-energy states of that symmetry.

This implies (cf. Eq. 3) that convergence will ultimately be to the lowest-energy state. However, the fixed-node approximation [1,7] used to treat the Fermi problem is of assistance here too. In the fixed-node approximation, the nodes of Ψ_T are used to divide $\underline{R}$-space into separate volume elements. The Schrödinger equation is solved separately in each of these elements. This results in a solution of the Schrödinger equation with added boundary conditions. Viewed this way, the Fermi problem is handled by forcing the generation of an antisymmetric state above the Bose ground state through the placement of nodes in the solution $\hat{\phi}$. In like manner, other excited states can be treated approximately by imposing additional nodes. The accuracy of the approximation will depend on how well these nodes are placed.

In treating excited states, traditional *ab initio* methods generate wave functions with the right number of nodes. Thus such wave functions are a good place to begin in searching for a function Ψ_T. We report preliminary results achieved with QMC when Ψ_T is a two-determinant SCF wave function. More details are given in Ref. 14. Tables 4 and 5 report our results on the first excited state of the He atom and of H_2 respectively. Two determinants are needed to obtain the required spatial symmetry. In the case of He, we have obtained 64% of the correlation energy for the 1s2s ^{1}S state. Though this appears low, we note that our final result is within 0.66 kcal/mol of the experimental energy. For H_2 we note that there is some basis set dependence. Nevertheless, a fairly simple basis set (double-zeta plus polarization) yields 75% of the correlation energy. We expect that better results will be obtained through the use of better optimized trial functions.

In summary, we have extended QMC to the study of energy derivatives, molecular properties, and molecular excited states. Preliminary results in these extended directions are encouraging. Further investigations are in progress.

References.

[1] P. J. Reynolds, D. M. Ceperley, B. J. Alder, and W. A. Lester, Jr., J. Chem. Phys. 77, 5593 (1982).

[2] J. W. Moskowitz, K. E. Schmidt, M. A. Lee, and M. H. Kalos, J. Chem. Phys. 77, 349 (1982).

[3] P. J. Reynolds, R. N. Barnett, and W. A. Lester, Jr., Int. J. Quant. Chem. Symp. 18, 709 (1984); F. Mentch and J. Anderson, J. Chem. Phys. 80, 2675 (1984); D. M. Ceperley and B. J. Alder, J. Chem. Phys. 81, 5833 (1984); R. N. Barnett, P. J. Reynolds, and W. A. Lester, Jr., J. Chem. Phys., 82, 2700 (1985).

[4] P. J. Reynolds, M. Dupuis, and W. A. Lester, Jr., J. Chem. Phys. 82, 1983 (1985).

[5](a) M. H. Kalos, Phys. Rev. 128, 1791 (1962); J. Comp. Phys. 1, 257 (1967); M. H. Kalos, D. Levesque, and L. Verlet, Phys. Rev. A 9, 2178 (1974); D. M. Ceperley in *Recent Progress in Many-Body Theories*, edited by J. G. Zabolitzky, M. de Llano, M. Fortes, and J. W. Clark (Springer-Verlag, Berlin, 1981); (b) D. M. Ceperley and M. H. Kalos in *Monte Carlo Methods in Statistical Physics,* K. Binder, ed. (Springer-Verlag, Berlin, 1979).

[6] J. M. Hammersley and D. C. Handscomb, *Monte Carlo Methods,* (Chapman and Hall, London, 1964).

[7] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. 45, 566 (1980);

[8] M. H. Kalos, Phys. Rev. A 2, 250 (1970).

[9] R. N. Barnett, P. J. Reynolds, and W. A. Lester, Jr., "Molecular Properties by Quantum Monte Carlo" *in preparation.*

[10] P. Pulay, in *Modern Theoretical Chemistry,* Vol. 4, H. F. Schaefer III, ed. (Plenum, New York, 1977); M. Dupuis and H. F. King, J. Chem. Phys. 68, 3998 (1978).

[11] P. Saxe, Y. Yamaguchi, and H. F. Schaefer III, J. Chem. Phys. 77, 5647 (1982).

[12] B. Holmer and D. M. Ceperley, *private communication*; B. Wells, P. J. Reynolds, and W. A. Lester, Jr., *unpublished*; B. H. Wells, Chem. Phys. Lett. 115, 89 (1985).

[13] W. Kolos and L. Wolniewicz, J. Chem. Phys. 43, 2429 (1965).

[14] R. N. Grimes, R. N. Barnett, P. J. Reynolds, and W. A. Lester, Jr., "Molecular Excited States with Fixed-Node Quantum Monte Carlo" *in preparation.*

[15] R. F. Borkman, Chem. Phys. Lett. 9, 624 (1971).

[16] W. Kolos and L. Wolniewicz, J. Chem. Phys. 41, 3674 (1963).

[17] F. Billingsley and M. Krauss, J. Chem. Phys. 60, 2767 (1974).

[18] D. E. Stogryn and A. P. Stogryn, Mol. Phys. 11, 371 (1966). See also Table 2 in Ref. [17].

[19] B. Liu, J. Chem. Phys. 58, 1925 (1973).

[20] Z. Ritter and R. Pauncz, J. Chem. Phys. 32, 1820 (1960).

[21] C. E. Moore, Natl. Bur. Standards Circ. No. 467, I (1948).

[22] R. Grimes, M. Dupuis, and W. A. Lester, Jr., *unpublished results*.

[23] R. Grimes, M. Dupuis and W. A. Lester, Jr., Chem. Phys. Lett. 110, 247 (1984).

[24] W. Kolos and L. Wolniewicz, J. Chem. Phys. 49, 404 (1968).

Table 1. Comparison of expectation values for properties of H_2. The properties studied are expectation values of the squared distance from the H_2 axis, along the H_2 axis, and from the center of the molecule (in bohr^2). The electric quadrupole moment, Q, (in $\text{esu}\cdot\text{cm}^2 \times 10^{-26}$) can be derived from the other expectation values. The trial function, Ψ_T, is a single-zeta-plus-bond SCF function, multiplied by electron-electron and electron-nuclear Jastrow functions. The function, $\hat{\phi}$, is the exact wave function in this case, since there are no nodes for the ground-state of H_2. However, a small bias due to the short-time approximation may be present. Here the time step is τ=0.01 au. "Approximate formula" refers to Eq. 4 of the text. Statistical uncertainty in the last significant figures is shown in parentheses.

Method	$(<x^2> + <y^2>)$	$<z^2>$	$<r^2>$	Q
Point Charge Model[a]	---	---	---	0.50
$<\Psi_T \mid A \mid \Psi_T>$	0.7715(9)	1.078(2)	2.621(3)	0.49(1)
$<\Psi_T \mid A \mid \hat{\phi}>$	0.7670(24)	1.047(4)	2.580(9)	0.56(2)
Approximate Formula	0.7625(49)	1.016(9)	2.539(18)	0.63(5)
$<\hat{\phi} \mid A \mid \hat{\phi}>$	0.7635(28)	1.025(5)	2.552(10)	0.61(3)
Exact[b]	0.7617	1.023	2.546	0.61

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[a] Ref. 15.

[b] Ref. 16.

Table 2. Comparison of values obtained for the electric quadrupole moment of N_2. The trial function, Ψ_T, is a double-zeta SCF function, multiplied by electron-electron and electron-nuclear Jastrow functions. Time steps of τ=0.0025 and 0.00125 au are used, with no noticable bias present. "Approximate formula" refers to Eq. 4 of the text. Statistical uncertainties are indicated in parentheses.

Method	Q (esu·cm $^2 \times 10^{-26}$)
Hartree-Fock[a]	-1.29
MCSCF[a]	-1.22
$<\Psi_T \mid Q \mid \Psi_T>$	-2.19(4)
$<\Psi_T \mid Q \mid \hat{\phi}>$	-1.80(10)
Approximate Formula	-1.41(20)
Experiment[b]	-1.4(1)

[a] Ref. 17.

[b] Ref. 18.

Table 3. Comparison of energy derivatives of H_2 at equilibrium with standard techniques. The QMC trial function consists of a double-zeta SCF wave function multiplied by an electron-electron correlation function of the form $\prod_{ij}(1-a\exp(br_{ij}+cr_{ij}^{d}))$. The parameters used are $a=0.48$, $b=0.54$, $c=0.33$, and $d=1.4$. Time steps ranging from τ=0.1 au to τ=0.005 au are used. The quoted results are extrapolations to τ=0. Energies are in hartrees and derivatives in hartrees/bohr. Statistical uncertainties are indicated in parentheses.

Method	E	dE/dρ
SCF[a]	-1.1335	0.0053
CI[b]	-1.1737	0.0007
QMC	-1.1745(12)	0.0009(24)
Exact[c]	-1.17447	0.0000

[a] Pulay in Ref. 10.
[b] Ref. 19.
[c] Ref. 13.

Table 4. Comparison of the energy of the first excited ^{1}S state of He with SCF and experiment. The SCF wave function, whose energy is shown in the table, is used as the QMC Ψ_T. The column headed %CE gives the percentage of the correlation energy recovered, and is computed relative to the SCF number in the first row of the table. A time step of τ=0.05 au is used. Statistical uncertainties are indicated in parentheses.

Method	E (h)	%CE	$\Delta(E-E_{\text{exp}})$ (kcal/mole)
SCF	-2.14307[a]	0	1.83
QMC	-2.14493(7)	64	0.66(4)
Experiment	-2.14598[b]	100	0.00

[a] Ref. 20.
[b] Ref. 21.

Table 5. Comparison of the energy of H_2 ($B\ ^1\Sigma_u^+$) at its equilibrium geometry with self-consistent field (SCF), configuration interaction (CI) and exact results. For QMC, two different trial functions are used. They are constructed from double-zeta (DZ) and double-zeta-plus-polarization (DZP) SCF functions. The column headed % CE gives the percentage of correlation energy recovered, and is computed relative to the SCF number in the first row of the table. A time step of τ=0.01 au is used. Statistical uncertainties are indicated in parentheses.

Method	$E(h)$	% CE	$\Delta(E-E_{exact})$ (kcal/mole)
SCF	-0.742 [a]	0	9.4
QMC (DZ)	-0.748(2)	41	5.6
QMC (DZP)	-0.753(1)	75	2.5
CI	-0.7553 [b]	90	0.9
Exact	-0.7567 [c]	100	0.0

[a] Ref. 22.
[b] Ref. 23.
[c] Ref. 24.

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