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Authors
Lester, W.A.
Reynolds, P.J.

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W.A. Lester, Jr. and P.J. Reynolds

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ACHIEVING CHEMICAL ACCURACY BY QUANTUM MONTE CARLO*

William A. Lester, Jr.[+] and Peter J. Reynolds
Materials and Molecular Research Division
Lawrence Berkeley Laboratory, University of California
Berkeley, California 94720

In order to better understand the processes resulting in the release of chemical energy, one needs a computational technique of high accuracy. One alternative approach to the current quantum chemistry techniques for molecular studies which holds great promise is the quantum Monte Carlo (QMC) method.[1-8] In this approach the many-body Schrödinger equation is re-interpreted as a diffusion equation. Simulation of an appropriate random-walk process enables one to calculate expectation values of molecular properties exactly, in principle, subject only to statistical errors (which may be made arbitrarily small). The computational effort with QMC rises roughly as N^2, where N is the number of electrons, making calculations on relatively large systems feasible. Using a simple, but accurate fixed-node approximation, the calculated total energy remains an upper bound to the true energy. The quality of the bound and the magnitude of the statistical error depend on an "importance function" which guides the diffusion through phase space. The location of the nodes of this function determines the accuracy which can be obtained. Even with very simple importance functions, we have obtained from 75-100% of the correlation energy of two to ten electron molecules (cf., Table I).

The QMC procedure applies equally well in situations away from the equilibrium geometry. In Table II we present some results for the ground-state energy of Li_2 at a few different nuclear separations. We chose the same importance function--with the same parameters--for all nuclear separations. Although this choice is not optimal, point-wise agreement with the exact results was nevertheless quite good.

Table I. Comparison of the total ground-state energy obtained in the fixed-node QMC procedure, with the estimated Hartree-Fock limit, CI, and "exact" energies. Except as noted, "exact" means the non-relativistic, Born-Oppenheimer energy, derived from experiment. The "quality" of each of the three importance functions (Ψ_I, Ψ_{II}, and Ψ_{III}) is also indicated, by giving the energy obtained from them in a variational calculation. Energies are in Hartrees. [After Ref. 7]

		H$_2$	LiH	Li$_2$	H$_2$O
Hartree-Fock		-1.1336 [a]	-7.987 [b]	-14.872 [c]	-76.0675 [d]
Ψ_I	variational	-1.1507±0.0009	-7.91±0.01	-14.85 ±0.03	-75.69 ± 0.03 [e]
	fixed-node	-1.1745±0.0008	-8.047±0.005	-14.985±0.005	-76.23 ± 0.02
Ψ_{II}	variational		-7.975±0.005	-14.900±0.004 [f]	-76.13 ±0.07 [e]
	fixed-node		-8.059±0.004	-14.991±0.007	-76.377±0.007
Ψ_{III}	variational	-1.162±0.001	-8.041±0.008	-14.95 ± 0.01	
	fixed-node	-1.174±0.001	-8.067±0.002	-14.990±0.002	
Best CI		-1.1731 [g]	-8.0647 [h]	-14.903 [i]	-76.3683 [j]
"Exact"		-1.17447... [k]	-8.0699 [l,n]	-14.9967 [m,n]	-76.4376 [d]

(a) Obtained with a nine term expansion in Ref. 9.
(b) Ref. 10.   (c) Ref. 11.
(d) Rosenberg and Shavitt in Ref. 12.
(e) Slater determinant part of wavefunction from Ref. 13.
(f) Variational energy from Moskowitz and Kalos in Ref. 8.
(g) Ref. 14. Of course, better correlated wavefunctions than CI exist for H$_2$. For example, Ref. 9 obtains E=-1.1744 from a 40 term expansion which includes r_{ij} explicitly, and the "exact" result of Ref. 15 also uses this method.
(h) Ref. 16.   (i) Refs. 17, 18.
(j) Meyer in Ref. 12.
(k) Ref. 15. This value is not derived from experiment, but directly from theory.
(l) Ref. 19.   (m) Ref. 20.
(n) Here the zero-point energy has not been subtracted; also the relativistic correction is assumed independent of $r_{\alpha\beta}$, and the Lamb shift has not been included.

Table II. Ground-state energies at selected nuclear separations for Li_2. Results of the fixed-node QMC calculation, obtained using the importance function Ψ_{II}, are compared with Hartree-Fock and "exact" energies (in Hartrees). Typical statistical uncertainty in the fixed-node results is 0.005 a.u. [After Ref. 7]

R (Bohr)	E_{HR} [a]	E_{F-N}	$E_{\text{"exact"}}$ [b]
3	-14.786	-14.905	-14.915
4	-14.853	-14.968	-14.983
5.05	-14.872	-14.991	-14.997
6	-14.869	-14.985	-14.992
7	-14.859	-14.976	-14.982

(a) Refs. 11, 17, 18.
(b) Ref. 20.

Our current work includes exploration of the following directions: (1) development and application of methods for excited states. In principle, at least certain excited-state calculations can be performed readily. For example, if the spin symmetry of a state is different from the ground state, this may be enforced on the calculated state Ψ by choosing an importance function Ψ_I with this same symmetry. The spin arrangement reflected in Ψ_I results in a significantly different nodal structure, and thus in different volume elements for the diffusion process than for the ground state. We have introduced the above considerations in calculations on the $^1A_1 - {}^3B_1$ energy splitting of methylene. In addition to the intrinsic interest in this value,[22] this calculation also gives insight into how well the QMC method obtains excited-state properties and to its sensitivity in calculating small energy differences. (2) Development of adaptive or self-improving Monte Carlo schemes. The goal is to feed back knowledge gained from a simulation with a Ψ_I into a improved function Ψ_I'. Such an algorithm should interatively correct a given starting Ψ_I to achieve the best possible importance function, even correcting the nodes. (3) As a more long-range goal, one wishes to eliminate the fixed-node constraint entirely. Such approaches,[21] although of great interest, are currently not practical for molecular calculations. The limitation arises from an inherent difficulty in reducing the variances with these algorithms. Attempts to overcome this problem create a new problem: the power law

dependence of the computation time on the number of electrons increases, making large calculations impractical. (4) Use of "differential" methods to obtain potential surfaces. In order to obtain a potential curve or surface, in principle, one must re-calculate the Born-Oppenheimer energy at various nuclear geometries. This is feasible (cf., Table II) however, a separate statistical error bar is associated with each calculation. This means that there is also an uncertainty in the shape of the potential curve—i.e., in the slope of the curve (or surface) joining the points. This problem derives largely from the separateness of the Monte Carlo calculations—involved—a different set of random numbers is used for each calculation but may be circumvented by calculating averages at nearby geometries using the same random numbers. Energies thus calculated are strongly correlated. Thus, the "differential" procedure can give more accurate relative energies than is possible from separate calculations of the absolute energies. In this way, accurate slopes (and hence forces), as well as energies, may be obtained. (5) Use of more accurate, compact importance functions. Our present importance functions Ψ_I all consist of a single Slater determinant multiplied by a fairly simple correlation factor. We have already found that (within the fixed-node approximation) we can obtain an additional 50% of the missing correlation energy simply by either enlarging the basis set slightly or optimizing further the parameters in Ψ_I. In this way we have brought the total correlation energy obtained to the order of 90% At the same time, this improvement in Ψ_I has led to an appreciable reduction in the fluctuations in the energy, and hence a reduction in the statistical error. We have studied the effect of a continued increase in the size of the basis set on the accuracy and on the precision of the calculated quantities, and find it to be negligible. However, to make computational time used more practical, we are investigating the reduction in statistical error which may be achieved by using different correlation functions. This reduction is needed in order to obtain energy differences in the kcal/mole range. To further improve absolute energies, we also wish to investigate other relatively compact forms of Ψ_I consisting of more than one Slater determinant.

An understanding of the improvement in the results which can be derived from improvements in Ψ_I, should enable one to obtain reliably between 90-95% (or better) of the correlation energy, and to extrapolate with some confidence the total energy and other properties of molecular systems, even without the self-adaptive or released-node approaches.

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