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QUANTUM MONTE CARLO FOR MOLECULES

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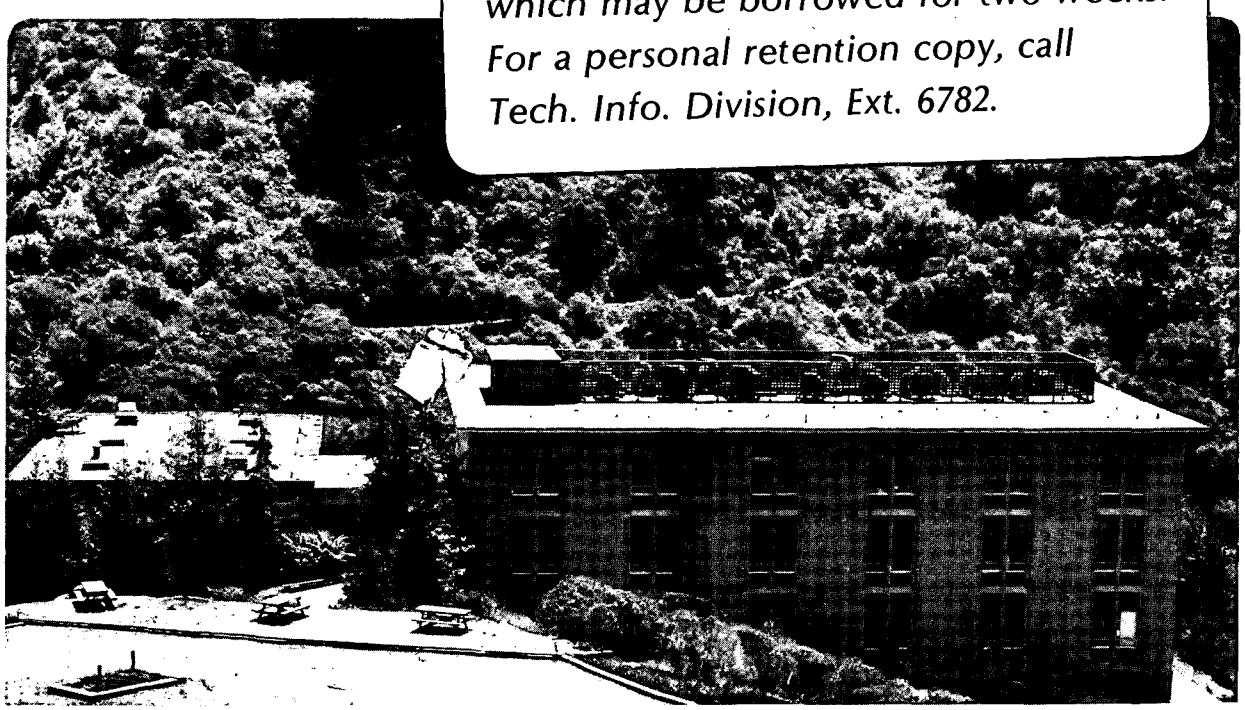

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Abstract

An alternative approach to conventional quantum chemistry techniques for molecular studies is described. This approach uses the quantum Monte Carlo method, which was developed and used primarily in nuclear and condensed-matter physics. In this approach the many-body Schrödinger equation is re-interpreted as a diffusion equation. Simulation of the appropriate random walk process allows one to calculate expectation values of molecular properties. In principle these expectation values can be calculated exactly, subject only to statistical errors (which may be made arbitrarily small). In preliminary work on small molecules (H_2, LiH, Li_2, and H_2O), we use a simple but accurate approximation to ease the treatment of Fermi statistics. In that approximation, the calculated total energy remains an upper bound to the true energy. How good the bound is, as well as the magnitude of the statistical error, depends on the quality of an "importance function" which guides the diffusion into more probable regions of phase space. With relatively simple importance functions, we obtain from 75-100% of the correlation energy of the above-mentioned molecules.

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Introduction

One of the important goals of theoretical molecular physics is to be able to calculate such properties as total energies, bond strengths, charge distributions, dipole moments, and potential energy surfaces, with a high degree of accuracy. The dominant techniques in use today for accurate molecular calculations are the multi-configuration self-consistent field (MCSCF) method in conjunction with configuration interaction (CI) expansions,[1] and many-body perturbation theory.[2] The CI expansions have the benefit of providing upper bounds to the total energy. Such expansions have been able to account for about 3/4 of the correlation energy of those small molecules that have been studied thus far. However, much interesting physics occurs on the energy scale of the unachieved correlation energy, and thus higher accuracy is greatly desired. Unfortunately, CI expansions converge slowly, and often in a non-uniform fashion. Furthermore, computational effort with the CI approach increases with somewhere between the fourth and fifth power of the number of electrons. This effectively limits the size of molecules the *ab initio* CI method can treat.

A direction that shows promise, and avoids the inherent limitations of expansion approaches, is the use of quantum Monte Carlo (QMC) methods.[3-16] These methods, developed and used primarily in nuclear and condensed-matter physics, differ radically from the conventional theoretical methods of molecular physics. One class of QMC methods is of the "exact" type, on which we focus here. Such approaches

actually solve the Schrödinger equation stochastically, giving a probability distribution proportional to the amplitude $\Psi(R)$ of the molecular system. Properties of interest are in effect "measured" as the system "evolves" under a dynamics whose steady-state is an eigenstate of the Schrödinger equation. Averages of the measured quantities in the steady-state yield the desired expectation values, subject only to statistical errors (which may be made arbitrarily small).

Until recently, however, QMC approaches suffered from large statistical errors, and were also unable to handle antisymmetric wavefunctions such as those of most molecules. Reduction of statistical error now has been achieved by use of importance sampling.[7,11-16] Recently, in work done in part at the National Resource for Computation in Chemistry (NRCC) at Lawrence Berkeley Laboratory, various schemes to treat Fermi statistics were developed[12,13] and applied to selected molecular systems.[14-16] In an initial effort,[14,15] we calculated the ground-state energies of H_2, LiH, Li_2, and H_2O by the QMC technique. We made a simple, though not severe, "fixed-node" approximation to treat Fermi statistics. This approximation may be removed however, as has been done for the homogeneous electron gas.[12] As we discuss below, the effect of this approximation is to shift the computed energy from the true value to a slightly higher value, as in a variational approach. The nature of the approximation is the imposition of a boundary condition which fixes the nodes (zeroes) of the wavefunction at the

nodes of an approximate trial wavefunction. We have found that even with relatively simple trial wavefunctions, and with modest computational effort, we are able to obtain from 75 - 100% of the correlation energy for each of the molecules treated--results at least as good as those obtained with the CI method. Furthermore, in this stochastic approach the computational complexity need only rise with the square of the number of electrons in the molecule.*

Reference 15 is the first--in effect, ground-breaking--calculation by these methods, for any but the simplest molecular systems. Given the relative ease of computation and the demonstrated high accuracy, this QMC method holds considerable promise for quantum chemistry. At this point, the method needs no longer be "proven" but must nevertheless be used for a variety of physical and chemical problems to gain widespread acceptance. Suitably generalized, we expect for example to calculate more accurate potential-energy surfaces than typically obtained by other methods, to remove the Born-Oppenheimer approximation in selected applications, and to calculate improved expectation values for other properties as well as the energy, both in the ground and excited states.

*The computational complexity goes as $AN^3 + BN^2$, where the cubic term comes from inverting the Slater matrix -- the matrix of orbitals forming the Slater determinant -- order N times (once for each electron moved), and the quadratic term comes from computing pairwise interactions. Generally $A \ll B$ making the algorithm effectively N^2 in the range of N we have treated. For N sufficiently large, the N^3 term would ultimately dominate. However, suitable modifications can be made, by use of sparse matrix algorithms, to eliminate this term. The computational complexity then goes as $B'N^2$. However, $B' > B$, making this modification costly for small N.

A brief description of the method follows in the succeeding two sections, and results of our previous studies are summarized in the final section.

Diffusion Interpretation of the Schrödinger Equation

Consider a Schrödinger-like equation in imaginary time:

$$-\frac{\partial \Psi(\underset{\sim}{R},t)}{\partial t} = [\frac{-\nabla^2}{2} + V(\underset{\sim}{R}) - E_T]\ \Psi(\underset{\sim}{R},t) \tag{1}$$

where $\underset{\sim}{R}$ is the 3N-dimensional vector specifying the coordinates of the N electrons of the molecule, and t is time measured in units of h. Further,

$$V(\underset{\sim}{R}) = \sum_{i>j} \frac{1}{r_{ij}} - \sum_{\alpha,i} \frac{Z_\alpha}{r_{i\alpha}} + \sum_{\alpha>\beta} \frac{Z_\alpha Z_\beta}{r_{\alpha\beta}} \quad , \tag{2}$$

is the potential energy of the molecule, $r_{ab} \equiv |\vec{r}_a - \vec{r}_b|$, where Roman indices label electronic coordinates and Greek indices label nuclear coordinates, Z_α is the charge on nucleus α, and E_T is a constant shift in the energy.

Equations (1) and (2) are written in atomic units*, where $e^2 = \hbar^2/m_e = 1$.

*Thus, energy is in hartrees, length in bohr, and charge in units of e.

The goal is to obtain a solution to the Schrödinger equation--say the ground-state molecular eigenfunction $\phi_0(\underset{\sim}{R})$ for the present--and expectation values of molecular properties. By expanding $\Psi(\underset{\sim}{R},t)$ in eigenfunctions $\phi_i(\underset{\sim}{R})$ of the Hamiltonian, and substituting into Eq. (1), one finds,

$$\Psi(\underset{\sim}{R},t) = \sum_i N_i e^{-(E_i-E_T)t} \phi_i(\underset{\sim}{R}) \quad . \tag{3}$$

The E_i are the energies corresponding to the states ϕ_i, and the coefficients N_i depend on the initial conditions. Thus, at sufficiently long times, t, only the leading term in the sum in Eq. (3) survives--all other terms decay faster. For example, if $N_0 \neq 0$ the asymptotic solution to Eq. (1) is

$$\Psi(\underset{\sim}{R},t) = N_0 e^{-(E_0-E_T)t} \phi_0(\underset{\sim}{R}) \quad . \tag{4}$$

If E_T is adjusted so that $E_T = E_0$, the asymptotic solution is a <u>steady-state</u> solution, and is the ground-state eigenfunction.

In order to solve Eq. (1), we first note that it is formally a diffusion-type equation. Thus Eq. (1) may be readily simulated.[8] In this interpretation $\Psi(\underset{\sim}{R},t)$ is the density of diffusers. Without the term $[E_T - V(\underset{\sim}{R})]\Psi(\underset{\sim}{R},t)$, we have an ordinary diffusion equation, which can be simulated by a random walk of diffusers through configuration space. On the other hand, the term $[E_T - V(\underset{\sim}{R})]\Psi(\underset{\sim}{R},t)$ alone on the right-hand side of Eq. (1) gives a rate equation

describing branching processes such as cascade showers and radioactive decay. Thus, in combination, the entire equation can be simulated as a diffusion process in which the number of diffusers increases or decreases locally, proportional to the density of diffusers already present. This branching process serves to increase the probability density in regions of favorable $V(\underset{\sim}{R})$.

A result of the diffusion interpretation, however, is that must be everywhere positive.* Thus, at first glance, the process is restricted to functions $\Psi(\underset{\sim}{R},t)$ that have no nodes. If Ψ does have nodes, and changes sign as in a Fermion ground-state, the apparent limitation of the diffusion analogy can be dealt with by treating positive and negative regions separately. If we do not allow diffusion between these regions, we have the fixed-node approximation, mentioned earlier.

Reduction of Statistical Error

Direct implementation of Eq. (1) through a random-walk process is inefficient. A given diffuser moves with equal probability in all directions; thus all regions of space are sampled with the same probability, even though the contributions to expectation values may be high in only a few localized regions of space. This straightforward approach thus leads to unnecessarily large variances (statistical errors) in the computation of averages. Furthermore, the branching process, which ultimately leads to an ensemble having the

*Of course one can always make an overall phase change in the wavefunction.

correct probability distribution, is also subject to large fluctuations. This results from the divergence of the term $[E_T - V(\underset{\sim}{R})]$ when any two particles come together. Such fluctuations also lead to slow convergence of the averages to their correct expectation values. Statistical errors resulting from these mechanisms can be reduced by the introduction of importance sampling.[17] Importance sampling enables one to incorporate any knowledge one has about the true solution into a "trial function" $\Psi_T(\underset{\sim}{R})$, and to use Ψ_T as a guide to diffuse more intelligently through configuration space. This will speed up convergence. Equation (1) corresponds to the case of complete ignorance, $\Psi_T = 1$.

The more information about the wavefunction that is known, and may be practically included in $\Psi_T(\underset{\sim}{R})$, the better Ψ_T will be able to guide the diffusion into regions of high probability. A convenient way of introducing importance sampling is described in Ref. 15. In the role of a guiding function for importance sampling, Ψ_T need not be exceptionally accurate. In fact, often a single determinant minimal basis set form for Ψ_T is sufficient. To allow explicitly for electronic correlation and to obtain the correct cusp behavior,* a Jastrow pair-

*The cusp condition is a requirement on a wavefunction Ψ that the leading singularity in $V(\underset{\sim}{R})$, when two particles come together, cancels when evaluating the energy $H\Psi/\Psi$. This leads to the conditions that, for two electrons

$$\frac{1}{\Psi}\frac{\partial\Psi}{\partial r_{ij}}\bigg|_{r_{ij}=0} = \begin{cases} 1/4 & \text{i,j like spins,} \\ 1/2 & \text{i,j unlike spins,} \end{cases} \quad \text{and} \quad \frac{1}{\Psi}\frac{\partial\Psi}{\partial r_{j\alpha}}\bigg|_{r_{j\alpha}=0} = -Z_\alpha \quad ,$$

for an electron and a nucleus. Thus, e.g., for opposite spins at small r_{ij}, $\Psi \propto \exp(r_{ij}/2)$, implying that the coefficient a in U_{ij} equals 1/2 (see later discussion).

correlation factor[18] of the form $\exp(\sum_{i>j} U_{ij})$ is useful, where $U_{ij} = ar_{ij}/(1 + br_{ij})$. This Padé form for U_{ij} is the simplest function having the desired properties that U_{ij} be linear in r_{ij} at small r_{ij} (for the cusp condition), and approaches a constant $[+ O(1/r_{ij})]$ at large r_{ij} (so that the wavefunction factors). Thus, a good choice of Ψ_T is

$$\Psi_T(\underset{\sim}{R}) = \det|D^{\alpha}_{ij}| \det D^{\beta}_{ij} |\exp(\sum_{i>j} U_{ij}) \quad , \tag{5}$$

where* $D^{s}_{ij} = \psi_i(\vec{r}_j;s)$, s is the spin state, and ψ_i is the <u>ith</u> molecular orbital (MO). The MO's can, for example, be linear combination of atomic orbitals (LCAOs). Since no integrals are computed explicitly, Slater-type orbitals (STO's) or other functional forms are as accessible as Gaussian orbitals (GTO's). The cusp condition, necessary for cancelling the singularity when two particles approach the same position, requires that a = 0.5 in the Jastrow factor; b and the parameters in the Slater determinant may be adjusted variationally (by Monte Carlo or in an SCF calculation) to achieve the lowest energy. More sophisticated Padé approximants for U_{ij} may also be taken.

The form of Eq. (5) is compact and reasonably accurate, as has been shown in variational calculations.[15,16,19] Thus, such a function should serve as a good guiding function in the QMC approach.

*If Ψ_T contains only a single Slater determinant, the full Slater matrix can always be block diagonalized into spin up and spin down submatrices by relabeling the coordinates.

Fermi Statistics and the Fixed-Node Approximation

The diffusion equation formulation requires that the density of diffusers be non-negative. In Eq. (1) this required that $\Psi(\underset{\sim}{R},t)$, and hence $\phi_0(\underset{\sim}{R})$, either have no nodes or that we treat the positive and negative regions of Ψ separately. On the other hand, with the introduction of importance sampling, it is $f(\underset{\sim}{R},t) = \Psi_T(\underset{\sim}{R})\Psi(\underset{\sim}{R},t)$ that plays the role of the density and which must not change sign. Thus, if Ψ_T were to have the exact nodes of the ground state, one could treat Fermi statistics immediately, since f would never change sign. Unfortunately, very little is known about the exact location of nodes in molecular systems.[20] From symmetry, one can only determine points on the nodal surface. Nevertheless, even without this knowledge, an exact simulation by a diffusion process is possible.[12-14]

In Ref. 15 we have employed the fixed-node approximation, in which the Schrödinger equation is solved in each nodally bounded volume of Ψ_T separately. This implies the boundary condition that $\Psi(\underset{\sim}{R},t) = 0$ at, and only at, the boundary of each volume.* In terms of the description of the wave equation as a diffusion equation with branching, this boundary condition means that the diffusers are absorbed at the nodes of Ψ_T. This modified diffusion process leads to the lowest energy solution with no internal nodes for each nodally bounded region of Ψ_T. The approximate ground state is then taken as the

*Because of the boundary condition imposed on Ψ by this approximation, the expansion of Eq. (3) must be in terms of eigenfunctions of H within the separate volume elements. Thus, the spectrum of eigenvalues E_i will not be exactly that of the true Fermion problem unless the nodes are correct.

antisymmetrized $\Psi(\underset{\sim}{R},t)$ obtained from the solution in the nodal region having the lowest energy. The energy expectation value calculated with the approximate density $f(\underset{\sim}{R}) = \Psi_T(\underset{\sim}{R})\ \Psi(\underset{\sim}{R})$ is then an upper bound to the true ground-state energy.[13,15] Thus the effect of the fixed-node approximation is to shift the energy expectation value from the exact answer to an upper-bound.* Nevertheless, as we discuss below, even very simple choices of Ψ_T in this approximation yield better than 80% of the correlation energy.

Solution by Monte Carlo

To obtain the asymptotic distribution $f_\infty(\underset{\sim}{R}) \equiv f(\underset{\sim}{R},t\to\infty)$, from which one can obtain $\Psi(\underset{\sim}{R})$, we begin with an arbitrary initial distribution $f(\underset{\sim}{R},0)$—for example, one created randomly, or one given by $|\Psi_T(\underset{\sim}{R})|^2$ obtained from an earlier variational QMC simulation. The time evolution of $f(\underset{\sim}{R},t)$ is given by

$$f(\underset{\sim}{R}',t+\tau) = \int d\underset{\sim}{R}\ f(\underset{\sim}{R},t)\ G(\underset{\sim}{R}\to\underset{\sim}{R}',\tau) \quad , \tag{6}$$

where the Green's function $G(\underset{\sim}{R}\to\underset{\sim}{R}',\tau)$ is the transition probability for moving the set of coordinates from $\underset{\sim}{R}$ to $\underset{\sim}{R}'$ in time τ. Thus G is a solution to the same differential equation, as f,** but with the boundary condition, $G(\underset{\sim}{R}\to\underset{\sim}{R}',0) = \delta(\underset{\sim}{R}'-\underset{\sim}{R})$.

*However, when the fixed-node approximation is made, $E_0 \leq \langle E_L\rangle \leq E_V$, where E_V is the variational energy $\langle\Psi_T|H|\Psi_T\rangle$, $E_L \equiv \Psi H\Psi_T/\Psi_T$, and the average is over the distribution f.

**The differential equation for f is essentially Eq. (1) multiplied through by Ψ_T.

For short times τ, an approximate Green's function solution is a Gaussian probability distribution whose mean drifts with a velocity proportional to $\nabla \ln |\Psi_T|^2$, and which spreads with time as $\sqrt{\tau}$. This distribution is sampled and is used to move the electrons in the Monte Carlo procedure. The Gaussian function has an exponential prefactor which grows or diminishes, depending on the relative sign of $E_L(\underset{\sim}{R}) \equiv H\Psi_T(\underset{\sim}{R})/\Psi_T(\underset{\sim}{R})$ and E_T. This change in "normalization" is carried out by creating or destroying entire electronic configurations, with a probability such that the average number of configurations at the next time step is $\exp(-\tau\{[E_L(\underset{\sim}{R})+E_L(\underset{\sim}{R}')]/2 - E_T\})$.

Thus to obtain a Monte Carlo solution for $\Psi(\underset{\sim}{R})$--i.e. to find the asymptotic distribution $f_\infty(\underset{\sim}{R})$ -- one applies Eq. (6) repeatedly for small τ, until t is sufficiently large. Once the equilibrium distribution for f is obtained, one may take any desired average over the configurations. For example, the total energy is obtained as the average value of the local energy:

$$\langle E_L \rangle \equiv \frac{\int f_\infty(\underset{\sim}{R})\ [H\Psi_T/\Psi_T]\ d\underset{\sim}{R}}{\int f_\infty(\underset{\sim}{R})\ d\underset{\sim}{R}}$$

$$= \frac{\int \Psi(\underset{\sim}{R}) H \Psi_T(\underset{\sim}{R})\ d\underset{\sim}{R}}{\int \Psi(\underset{\sim}{R})\Psi_T(\underset{\sim}{R})\ d\underset{\sim}{R}} = \frac{\int \Psi_T(\underset{\sim}{R}) H \Psi(\underset{\sim}{R})\ d\underset{\sim}{R}}{\int \Psi(\underset{\sim}{R})\Psi_T(\underset{\sim}{R})\ d\underset{\sim}{R}} = \varepsilon \quad , \tag{7}$$

where ε is the eigenvalue corresponding to the eigenfunction $\Psi(R)$. Note that ε is <u>not</u> the variational energy of Ψ_T.

Results and Discussion

In Ref. 15 we presented the ground-state energies of the molecules H_2, LiH, Li_2, and H_2O, using the fixed-node approximation. The results presented there were obtained for several different choices of the importance function Ψ_T. In particular, for each molecule we used either two or all three of the following: a Jastrow electron-electron pair-correlation function multiplied by a Slater determinant of molecular orbitals constructed from (I) a minimal basis set of STO's, (II) a somewhat enhanced basis set and/or optimized version of (I), and (III) localized Gaussian-like orbitals. Importance functions of type III contain an additional electron-nuclear Jastrow factor, which eliminates the singularity when an electron approaches the position of a nucleus.

Details on the importance functions are given in Ref. 15. The total energies corresponding to these choices are presented in Table I. For each molecule we compare the fixed-node QMC results with (a) the Hartree-Fock energy, (b) the best CI calculation, and (c) the "exact" clamped (i.e., fixed nuclei) non-relativistic result. In addition, to gain an appreciation for the intrinsic quality of Ψ_T, i.e., independent of the fixed-node procedure, we give the variational energy corresponding to each Ψ_T. For most of the wavefunctions, the parameters have only been partially optimized, both to save computer time and to demonstrate the strength of the fixed-node procedure.

Table I. Comparison of the total ground-state energy obtained with the fixed-node QMC procedure, versus 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. 15]

	H_2	LiH	Li_2	H_2O
Hartree-Fock	-1.1336 [a]	-7.987 [b]	-14.872 [c]	-76.0675 [d]
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
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
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	-1.1737 [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. 21.
(b) Ref. 22. (c) Ref. 23.
(d) Rosenberg and Shavitt in Ref. 24.
(e) Slater determinant part of wavefunction from Ref. 25.
(f) Variational energy from Moskowitz and Kalos in Ref. 16.
(g) Ref. 26. Of course, better correlated wavefunctions than CI exist for H_2. For example, Ref. 21 obtains E=-1.1744 from a 40 term expansion which includes r_{ij} explicitly, and the "exact" result of Ref. 27 also uses this method.
(h) Ref. 28. (i) Refs. 29, 30.
(j) Meyer in Ref. 24.
(k) Ref. 27. This value is not derived from experiment, but directly from theory.
(l) Ref. 31. (m) Ref. 32.
(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.

Whereas the inexactness of a usual variational calculation is due to the inexactness of Ψ_T, the inexactness of the fixed-node QMC results is due solely to the approximation made in forcing the state to have the inexact nodes of Ψ_T. In Table I, we see that numerically the fixed-node approximation appears quite good. For a given Ψ_T, the fixed-node QMC energies are much superior to the variational energies, yielding approximately 90% of the energy missing in the variational treatment. In fact, the fixed-node procedure may be thought of as a stochastic method of "correcting" the variational wavefunction Ψ_T through a branching process.

For H_2, where the ground state has no nodes--since there is only one electron in each spin state--the fixed-node QMC results are exact.* The only uncertainty is statistical. On the other hand, the same trial function (e.g., Ψ_I) used variationally gives only about 50% of the correlation energy. For LiH, and Li_2 the three trial functions, used as variational wavefunctions, range from considerably worse than Hartree-Fock to considerably better. Note, however, that in each case--regardless of the quality of the starting Ψ_T--the fixed-node calculation picks up almost 90% of the discrepancy between the variational energy and the exact energy. Finally, for H_2O the variational quality of neither of the two trial functions used is especially good. Nevertheless, with the fixed-node QMC these trial functions yield ~80% of the energy difference between the variational and exact energies.

*In the current procedure there is a small time-step error due to the finiteness of τ. This error can however be eliminated.

The results presented in Table I represent only a few hours of computer time per molecule on a CDC 7600. There is, however, no fixed amount of computer time that is necessary; more or less can be used. The effect of a longer computer run is to increase the precision with which the computed averages, such as the energy, are known. The error bars obtained are the standard deviations of the mean. By running as long as we have, we have reduced these error bars sufficiently that for each Ψ_T the effect of the fixed-node approximation becomes visible. The approximation manifests itself when the statistical error bars do not encompass the exact answer. For H_2, however, where there is no fixed-node approximation, reduction of the statistical error gives the exact answer more and more precisely.

Considering the simplicity of our trial functions, it is perhaps remarkable that by applying the fixed-node procedure we obtained (e.g., with Ψ_{III}) between 95% and 100% of the correlation energy; presently the statistical error is about 2% of the correlation energy. We note that for all the above molecules the fixed-node procedure gave a fairly constant fraction of the energy missed by the variational wavefunction. Thus even the simplest trial function, Ψ_I, was able to achieve from 50-90% of the correlation energy. Furthermore, the fixed-node procedure with our best choice of Ψ_T did at least as well as the CI calculation. As is clear from Table I, the results improve by choosing better Ψ_T's, since in general these will more accurately represent the nodes of the true wavefunction. Thus there is potential for still higher absolute accuracy, in addition to the reduction in

statistical error which may be achieved by running the program longer. By release of the fixed-node constraint it should be possible to achieve 100% of the correlation energy, even for the simplest trial functions.

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 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. 15]

R (Bohr)	E_{H-F} [a]	E_{F-N}	$E_{"exact"}$ [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. 23, 29, 30.
(b) Ref. 32.

REFERENCES

1. H. F. Schaefer, Electronic Structure of Atoms and Molecules (Addison-Wesley, Reading, MA, 1972).
2. R. J. Bartlett, Ann. Rev. Phys. Chem. 32, 359 (1981) and references therein.
3. N. Metropolis and S. M. Ulam, J. Amer. Statist. Assoc. 44, 247 (1949).
4. M. H. Kalos, Phys. Rev. 128, 1791 (1962); J. Comp. Phys. 2, 257 (1967).
5. W. L. McMillan, Phys. Rev. A138, 442 (1965).
6. R. C. Grimm and R. G. Storer, J. Comp. Phys. 7, 134 (1971).
7. M. H. Kalos, D. Levesque and L. Verlet, Phys. Rev. A 9, 2178 (1974).
8. J. B. Anderson, J. Chem. Phys. 63, 1499 (1975); ibid 65, 4121 (1976).
9. D. M. Ceperley, G. V. Chester, and M. H. Kalos, Phys. Rev. B 16, 3081 (1977).
10. D. M. Ceperley and M. H. Kalos, in Monte Carlo Methods in Statistical Physics, K. Binder ed. (Springer Verlag, Berlin, 1979), pp. 145-97.
11. J. B. Anderson, J. Chem. Phys. 73, 3897 (1980); F. Mentch and J. B. Anderson, J. Chem. Phys. 74, 6307 (1981).
12. D. M. Ceperley and B.J. Alder, Phys. Rev. Lett. 45, 566 (1980).
13. D. M. Ceperley, "The Stochastic Solution of the Many-Body Schrödinger Equation for Fermions" in Recent Progress in Many-Body Theories, J. G. Zabolitzky, M. de Llano, M. Fortes, and J. W. Clark eds., (Springer-Verlag, 1981) pp. 262-9.

14. B. J. Alder, D. M. Ceperley and P. J. Reynolds, J. Phys. Chem. 86, 1200 (1982).

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

16. J. W. Moskowitz and M. H. Kalos, Int. J. Q. Chem. 20, 1107 (1981) and J. W. Moskowitz, K. E. Schmidt, M. A. Lee, and M. H. Kalos, J. Chem. Phys. 76, 1064 (1982); J. W. Moskowitz, K. E. Schmidt, M. A. Lee, and M. H. Kalos, preprint (1982).

17. J. M. Hammersley and D. C. Handscomb, Monte Carlo Methods, (Chapman and Hall, 1964) pp. 57-9.

18. R. Jastrow, Phys. Rev. 98, 1479 (1955); R. B. Dingle, Phil. Mag. 40, 573 (1949).

19. Good results have also been obtained with other forms for the pair-correlation function. See, e.g., C.C.J. Roothaan and A. W. Weiss, Rev. Mod. Phys. 32, 194 (1960); W. Kolos and C.C.J. Roothaan, Rev. Mod. Phys. 32, 205 (1960); and W. A. Lester Jr. and M. Krauss J. Chem. Phys 41, 1407 (1964); ibid 44, 207 (1966).

20. R. J. White and F. H. Stillinger, Phys. Rev. A 3, 1521 (1971); D. J. Klein and H. M. Pickett, J. Chem. Phys. 64, 4811 (1976).

21. W. Kolos and C.C.J. Roothaan, Rev. Mod. Phys. 32, 219 (1960).

22. P. E. Cade and W. M. Huo, J. Chem. Phys. 47, 614 (1967).

23. G. Das and A. C. Wahl, J. Chem. Phys. 44, 87 (1966).

24. B. J. Rosenberg and I. Shavitt, J. Chem. Phys. 63, 2162 (1975); W. Meyer, Int. J. Q. Chem., Symp. No. 5, 341 (1971).

25. S. Aung, R. M. Pitzer, and S. I. Chan, J. Chem. Phys. 49, 2071 (1968).

26. B. Liu, J. Chem. Phys. 58. 1925 (1973).

27. W. Kolos and L. Wolniewicz, J. Chem. Phys. 41, 3663 (1964); ibid 43, 2429 (1965); ibid 49, 404 (1968).

28. W. Meyer and P. Rosmus, J. Chem. Phys. 63, 2356 (1975).

29. G. Das, J. Chem. Phys. 46, 1568 (1967).

30. D. D. Konowalow and M. L. Olson, J. Chem. Phys. 71, 450 (1979).

31. G. C. Lie and E. Clementi, J. Chem. Phys. 60, 1275 (1974).

32. G. C. Lie and E. Clementi, J. Chem. Phys. 60, 1288 (1974).

33. See for example C. C. Hayden, D. M. Neumark, K. Shobatake, R. K. Sparks, and Y. T. Lee, J. Chem. Phys. 76, 3607 (1982).

34 W. Kolos and L. Wolniewicz, Rev. Mod. Phys. 35, 473 (1963).

35. D. M. Ceperley, private communication.

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