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Monte Carlo Calculations of Atoms and Molecules

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The variational and Green's function Monte Carlo (GFMC) methods can treat many interesting atomic and molecular problems. These methods can give chemical accuracy for up to 10 or so electrons. The various implementations of the GFMC method, including the domain Green's function method and the short-time approximation, are discussed. Results are presented for several representative atoms and molecules.

KEY WORDS: Electrons structure; Monte Carlo; Green's function; fixed node; correlation energy; excited states.

1. INTRODUCTION

We will explain briefly the variational and Green's function Monte Carlo (GFMC) methods used by our group at New York University and give some representative results for atoms and molecules. The Hamiltonian is that of the nonrelativistic Schrödinger equation within the Born–Oppenheimer approximation. In atomic units

$$\begin{aligned} H &= -\frac{1}{2}\sum_i \nabla_i^2 - \sum_{i,j} \frac{Z_j}{|\vec{r}_{N_j} - \vec{r}_i|} + \sum_{i<j} \frac{1}{|\vec{r}_i - \vec{r}_j|} \\ &= -\frac{1}{2}\nabla_R^2 + V(R) \end{aligned} \tag{1}$$

where $\vec{r}_i$ is the electron position, $\vec{r}_{N_i}$ the fixed position of the nucleus i, and Z_i is the charge of the nucleus i. Hereafter, $\vec{R}$, $\vec{R}'$, and $\vec{R}''$ etc. will express the $3N$ coordinates of the N electrons.

The variational and GFMC methods can be used to calculate the expectation value of any ground-state quantity. We will give results for the

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correlation energy, the excited state splitting, and potential surface. The GFMC calculations will be using the method often known as domain Green's function.(1,2,3) The variational method is used to get initial results and to generate starting Monte Carlo walkers for the GFMC calculations.(4)

2. THE VARIATIONAL METHOD

The variational method is given by calculating the expectation value of the Hamiltonian and noting that it is an upper bound to the exact ground-state energy E_0

$$
\begin{aligned}
E_0 &\leqslant \frac{\int d\vec{R}\, \Psi_T^*(\vec{R})\, H \Psi_T(\vec{R})}{\int d\vec{R}\, \Psi_T^*(\vec{R})\, \Psi_T(\vec{R})} \\
&= \int d\vec{R}\, \frac{H\Psi_T^*(\vec{R})}{\Psi_T^*(\vec{R})} \frac{\Psi_T^*(\vec{R})\, \Psi_T(\vec{R})}{\int d\vec{R}'\, \Psi_T^*(\vec{R}')\, \Psi_T(\vec{R}')}
\end{aligned}
\tag{2}
$$

The second evaluation of the integral is easily calculated using the Metropolis et al. method(5) giving a low variance answer since $H\Psi_T^*(\vec{R})/\Psi_T^*(\vec{R})$ will be nearly constant if $\Psi_T(\vec{R})$ is close to the true ground-state wave function.

The integration can be implemented using a standard single-particle move Metropolis Monte Carlo method; however, it is convenient to calculate it using a slightly generalized multi-particle move method. This method utilizes a directed sampling (or force bias or smart Monte Carlo) method that has been discovered and described many times in the literature.(6) The a priori transition probability for a move of each particle within a box of side δ from the position $\vec{R}_i = (x_1{}^i, x_2{}^i, \ldots, x_{3N}{}^i)$ to $\vec{R}_j$ is taken to be

$$
\begin{aligned}
T_{i\to j} &= \prod_{l=1}^{3N} \{1 + \operatorname{sign}[\min(2\alpha/\delta, |F_l|), F_l](x_l{}^j - x_l{}^i)/\delta^3\} \\
&\approx \frac{\Psi_T(\vec{R}_j)}{\Psi_T(\vec{R}_i)}
\end{aligned}
\tag{3}
$$

with $0 \leqslant \alpha \leqslant 1$. This is just a linear approximation to the ratio of the wave functions at the new and old positions. The sign and the minimum functions are used to ensure that $T_{i\to j}$ is a valid probability density. The acceptance probability is

$$
A_{i\to j} = \operatorname{Min}\left(1, \frac{T_{j\to i}\Psi_T^2(\vec{R}_j)}{T_{i\to j}\Psi_T^2(\vec{R}_i)}\right) \tag{4}
$$

and a value of $\alpha \approx 0.8$ is found to be nearly optimal. The virtue of this method is that the same routines can be used to calculate the wave function and its derivatives for both the variational and the GFMC methods. For the small ($N \leqslant 10$) systems we have studied, this multi-particle technique is nearly as efficient as the standard Metropolis method.

The variational trial functions we take are usually of the form

$$\Psi_T(\vec{R}) = \prod_{i<j} f(|\vec{r}_i - \vec{r}_j|)\, \Phi(\vec{R}) \tag{5}$$

where the Jastrow function

$$f(r) = \exp\left(\frac{ar}{1+br}\right) \tag{6}$$

with a and b variational parameters, gives the correct coulomb cusp condition and heals smoothly to a constant at large r. The model function $\Phi(\vec{R})$ is typically a Hartree–Fock self-consistent field wave function or a very small (typically 2- to 10-configuration) configuration interaction wave function. All orbitals are taken to be a linear combination of Slater orbitals.

3. THE GFMC METHOD

The GFMC method was first applied to a nontrivial atomic problem by Kalos.(7) Many improvements have been made since the initial calculation.(1,2,8) I will describe here our current GFMC calculations. Two different forms for the GFMC method are used, and these correspond to time-dependent and resolvent methods in standard many-body perturbation theory. The corresponding integral equations for the Schrödinger equation are

$$\psi(\tau + \Delta\tau) = \exp[-(H - E_T)\,\Delta\tau]\,\psi(\tau) \tag{7}$$

and

$$\psi^{n+1} = \left[\frac{E_T + E_C}{H + E_C}\right] \psi^n \tag{8}$$

with $E_C + E_0 > 0$. Both of these methods, when iterated many times, converge exponentially to the lowest state of H not orthogonal to the starting wave function. It is clear that any decreasing function of H could be used as a propagator to converge to the ground state of H. E_T and E_C are constants. The value of E_T is chosen to be a good approximation to the ground state energy and the value of E_C is chosen so that the spectrum of $H+E_C$ is positive. Further adjustments in E_C affect the efficiency of the algorithm but not the result.

In the present calculations the second or resolvent form of the Green's function is used. However, it is calculated from the equation

$$\frac{1}{H+E_C}=\int_0^{\infty} d\tau\, e^{-(H+E_C)\tau} \tag{9}$$

The integration over τ is done by Monte Carlo. After convergence it is easy to see that the sampled times τ have a Poisson distribution with an average value of $n/(E_0+E_C)$ after n steps. E_C controls the average time step. If E_C is large, the time step is small.

The energy expectation value is calculated in two equivalent ways. The mixed energy is

$$E_M=\frac{\int d\vec{R}\, \Psi_T^*(\vec{R})\, H\psi^n(\vec{R})}{\int d\vec{R}\, \Psi_T^*(\vec{R})\, H\psi^n(\vec{R})} \tag{10}$$

It is convenient to operate H to the left in (10). If the initial wave function $\psi^{n=0}$ is equal to the trial function $\Psi_T(\vec{R})$ then, by commuting H with $1/(H+E_C)$ it is earily shown that

$$E_M=\frac{\int d\vec{R}\, \psi^{n/2}(\vec{R})\, H\psi^{n/2}(\vec{R})}{\int d\vec{R}\, \psi^{n/2}(\vec{R})\, \psi^{n/2}(\vec{R})} \tag{11}$$

Since this is a variational integral, E_M is an upper bound to E_0 for all n and as $n\rightarrow\infty$, $E_M=E_0$.

The growth energy is obtained by looking at the change in the normalization of the wave function. As can be seen from (7) and (8), once ψ has converged, the normalization will be unchanged during further iteration if E_T is chosen to be E_0. The ratio of the input to output normalizations gives an energy equivalent to but with higher variance than the mixed energy.

The Green's function is not known and must be calculated or sampled. This is accumplished by writing the following identity

$$\frac{1}{H+E_C}=\frac{1}{H_U+E_C}+\frac{1}{H_U+E_C}(H_U-H)\frac{1}{H+E_C} \tag{12}$$

Equation 12 is proved by writing H_U-H as $(H_U+E_C)-(H+E_C)$ and canceling terms. The Hamiltonian H_U represents a set of solvable Hamiltonians. At each iteration of (12) a different Hamiltonian may be used. The terms on the right-hand side of (12) are all analytically known functions when (12) is iterated. To sample the full Green's function $1/(H+E_C)$, we sample the sum of terms indicated by the right-hand side of (12). A similar equation can be used for the time-dependent Green's function of (7).

To make further progress, it is convenient to work in R space where the calculations are actually done. The R space Green's functions for the Hamiltonians H and H_U

$$G(\vec{R}, \vec{R}') = \langle \vec{R} | \frac{1}{H+E_C} | \vec{R}' \rangle \tag{13}$$

$$G_U(\vec{R}, \vec{R}') = \langle \vec{R} | \frac{1}{H_U+E_C} | \vec{R}' \rangle \tag{14}$$

satisfy the equations

$$(H+E_C)\, G(\vec{R}, \vec{R}') = \delta(\vec{R}-\vec{R}') \tag{15}$$

$$(H_U+E_C)\, G_U(\vec{R}, \vec{R}') = \delta(\vec{R}-\vec{R}') \tag{16}$$

A simple form for H_U is

$$H_U = -\tfrac{1}{2}\nabla_R^2 + U \tag{17}$$

with U independent of R. It is convenient to enforce the boundary condition that $G_U(\vec{R}, \vec{R}')$ goes to zero on the boundary of a domain. This domain is usually taken to be defined by allowing each particle to move in a sphere of a different but fixed radius about its current position. The use of a domain for $G_U(\vec{R}, \vec{R}')$ often looks strange at first sight. However, it is also often used in another guise in lattice calculations. For example, a checkerboard breakup of the Hamiltonian can be viewed as a domain since it restricts the number of final states that can be reached by the propagator. It is then only necessary to have H_U be a good approximations to H within this restricted domain to have good convergence properties of (12).

Equation 12 in R space becomes

$$\begin{aligned} G(\vec{R}, \vec{R}') = G_U(\vec{R}, \vec{R}') &- \int_S d\vec{R}''\, G(\vec{R}, \vec{R}'')[-\hat{n}\cdot\nabla G_U(\vec{R}'', \vec{R}')] \\ &+ \int_V d\vec{R}''\, G(\vec{R}, \vec{R}'')[U - V(\vec{R}'')]\, G_U(\vec{R}'', \vec{R}') \end{aligned} \tag{18}$$

The second and third terms on the right-hand side come about from the difference $H_U - H$. The second term is the difference in the kinetic energies and becomes an integral over the surface of the domain of G_U. The $-\hat{n}\cdot\nabla$ operator is the gradient normal to the surface. The third term is the difference in potential energy and is an integral over the volume of the domain of G_U. This equation represents the propagation of walkers by $G(\vec{R}, \vec{R}')$. The first term is propagation by G_U. In the second term, the walker propagates from $\vec{R}'$ to $\vec{R}''$ where it scatters off the surface of the domain and then propagates from $\vec{R}''$ to $\vec{R}$ via the full Green's function. In the third term the walker scatters off the difference in the potential between H_U and H. If U is chosen such that for all $\vec{R}''$ within the domain, $U > V(\vec{R}'')$, all the terms on the right-hand side of (18) are positive and can be viewed as probability densities. In this case $G(\vec{R}, \vec{R}')$ has been expressed as a sum of probability densities and can be sampled by first selecting a term with probability given proportional to its normalization and then sampling $\vec{R}$ from that term.

It is instructive to look at an approximation to (18), good in the limit of large E_C, which is equivalent to the short-time approximation. If the domain is taken to be $V(\vec{R}')$ and E_C is taken very large, only small τ in (9) will contribute. Therefore $G_U(\vec{R}, \vec{R}')$ becomes sharply peaked about $\vec{R} = \vec{R}'$ and $V(\vec{R}) \approx V(\vec{R}')$. The third term in (18) can be made arbitrarily small by increasing E_C. By dropping this term, a large E_C approximation is obtained. At this point (8) can be iterated and the resulting integrals done with Metropolis Monte Carlo, recovering a path-integral formulation. Instead we sum the series indicated by (18) while doing the integrals with standard Monte Carlo methods. The selection of the sphere radii about each electron for the domain will affect the efficiency but not the final answer.

Importance sampling methods greatly decrease the variance of the final answer. We give here a simple argument for taking the importance function equal to the trial function. Equation 8 becomes, in R space

$$\psi^n(\vec{R}) = (E_T + E_C) \int d\vec{R}'\, G(\vec{R}, \vec{R}')\, \psi^{n-1}(\vec{R}') \tag{19}$$

After convergence to the ground state, we want a low-variance method to calculate the eigenvalue. It is simplest to look at the growth energy for this analysis since the variance of the mixed energy will be zero if the exact ground-state wave function is used for Ψ_T. A low variance for the growth energy means that a walker at $\vec{R}'$ should produce one walker at some position $\vec{R}$; that is, there should be no branching. After convergence, the iterated wave function becomes equal to the ground state wave function

$$\psi^{n-1}(\vec{R}') = \psi_0(\vec{R}') \tag{20}$$

The correct importance function is obtained from the solution of the adjoint equation run backward from the target to the current point. Equation 19 defines a self-adjoint problem so that the importance function should be ψ_0. To see this, the Green's function is run backward. The only part of the Green's function that contributes in this limit is $\psi_0(\vec{R})\,\psi_0(\vec{R}')/(E_0+E_C)$. The interesting part of the integral in (19) is

$$\psi^n(\vec{R})=\frac{E_T+E_C}{E_0+E_C}\int d\vec{R}'[\psi_0(\vec{R})\;\psi_0(\vec{R}')]\;\psi_0(\vec{R}') \tag{21}$$

If $\vec{R}'$ is sampled from $\psi_0(\vec{R}')/\int d\vec{R}''\,\psi_0(\vec{R}'')$, the value of the remainder of the integral depends on $\vec{R}'$ and will not produce one walker in the next iteration. However, if $\vec{R}'$ is sampled from $\psi_0^2(\vec{R}')$, all the $\vec{R}'$ dependence of (21) is sampled and a low-variance result can be obtained. Since ψ_0 is not known, the trial function is taken as the importance function. The interesting part of (19) can then be rewritten as

$$\psi^n(\vec{R})\;\Psi_T(\vec{R})=\frac{E_T+E_C}{E_0+E_C}\int d\vec{R}'\left[\Psi_T(\vec{R})\,\psi_0(\vec{R})\frac{\psi_0(\vec{R}')}{\Psi_T(\vec{R}')}\right]\Psi_T(\vec{R}')\,\psi^{n-1}(\vec{R}') \tag{22}$$

and if $\Psi_T(\vec{R})=\psi_0(\vec{R})$ and $E_T=E_0$, a zero-variance method results since each walker produces exactly one walker in the next iteration. The inclusion of importance sampling is made by substituting

$$\psi^n(\vec{R})\to\Psi_T(\vec{R})\,\psi^n(\vec{R})$$
$$G(\vec{R},\vec{R}')\to\Psi_T(\vec{R})\,G(\vec{R},\vec{R}')/\Psi_T(\vec{R}')$$

in (18) and (19). The inclusion of importance sampling also makes the calculation of the mixed energy simpler and less biased.

An algorithm for the actual sampling of the importance sampled Green's function equation

$$\begin{aligned}(E_T+E_C)\frac{\Psi_T(\vec{R}')}{\Psi_T(\vec{R})}G(\vec{R}',\vec{R})&=(E_T+E_C)\frac{\Psi_T(\vec{R}')}{\Psi_T(\vec{R})}G_U(\vec{R}',\vec{R})\\&+\int_S d\vec{R}(E_T+E_C)\frac{\Psi_T(\vec{R}')}{\Psi_T(\vec{R}'')}G(\vec{R}',\vec{R}'')\frac{\Psi_T(\vec{R}'')}{\Psi_T(\vec{R})}[-\hat{n}\cdot\nabla G_U(\vec{R}'',\vec{R})]\\&+\int_V d\vec{R}''\frac{\Psi_T(\vec{R}')}{\Psi_T(\vec{R}'')}G(\vec{R}',\vec{R}'')[U-V(\vec{R}'')]\frac{\Psi_T(\vec{R}'')}{\Psi_T(\vec{R})}G_U(\vec{R}'',\vec{R})\end{aligned} \tag{23}$$

will now be given. It is simplest to first explain how (23) would be sampled in the large E_C or short-time approximation and then generalize to the full sampling of (23). Since (23) is a recursive equation, it is convenient to place the Monte Carlo walkers on a push-down , pop-up stack. Each entry in the stack is a walker consisting of the $3N$ coordinates of the N electrons. In practice it is useful to cary along various other quantities such as the value of the current potential energy and various derivatives of the trial wave function as well to make the calculation efficient. Here we will assume that these quantities are calculated as needed to make the exposition more clear. It should be noted that data structures other than a stack may be more useful for different machine architectures. In particular, on parallel machines a circular queue structure leads to a more efficient program.

Initially, a full stack of walkers is generated by sampling from $\Psi_T^2(\vec{R})$ in a variational calculation or from sampling $\Psi_T(\vec{R})\,\psi^{n-1}(\vec{R})$ from the last iteration. I will call this the old stack. Walkers will be propagated to a new stack. Initially, it is empty.

In the large E_C limit only the first term of (23) survives, as explained earlier. In this case, sampling (23) is accomplished by the following steps

1. Pop a walker off the old stack. Its position defines the coordinates $\vec{R}$ in (23). Select U (normally select $U = V(\vec{R})$).
2. Sample a time step. This is accomplished by recalling that

$$\begin{aligned}\frac{\Psi_T(\vec{R}')}{\Psi_T(\vec{R})}G(\vec{R}',\vec{R}) &= \frac{\Psi_T(\vec{R}')}{\Psi_T(\vec{R})}\langle\vec{R}'|\frac{1}{H+E_C}|\vec{R}\rangle\\ &= \frac{\Psi_T(\vec{R}')}{\Psi_T(\vec{R})}\int_0^\infty d\tau\langle\vec{R}'|\exp(-(H+E_C)\tau)|\vec{R}\rangle\\ &\equiv \frac{\Psi_T(\vec{R}')}{\Psi_T(\vec{R})}\int_0^\infty d\tau\, G_U(\vec{R}',\vec{R},\tau)\end{aligned} \tag{24}$$

   Here $\{\Psi_T(\vec{R}')/[\Psi_T(\vec{R})]\}\, G_U(\vec{R}',\vec{R},\tau)$ will be approximately a Gaussian with a drift term. By approximately integrating $\{\Psi_T(\vec{R}')/[\Psi_T(\vec{R})]\}\, G_U(\vec{R}',\vec{R},\tau)$ over $\vec{R}'$, a probability density for selecting a time τ results; τ is then sampled from this density.
3. Now that τ is known, $\vec{R}'$ is sampled from an approximation to $\{(E_T+E_C)[\Psi_T(\vec{R}')/[\Psi_T(\vec{R})]\}\, G_U(\vec{R}',\vec{R},\tau)$.
4. Calculate a weight. This is given by the ratio

$$W = \frac{[(E_T+E_C)\{\Psi_T(\vec{R}')/\Psi_T(\vec{R})\}\, G_U(\vec{R}',\vec{R},\tau)]}{P(\vec{R}',\tau)} \tag{25}$$

   where $P(\vec{R}',\tau)$ is the probability density from which $\vec{R}'$ and τ are sampled.

5. Calculate $N = \mathrm{int}(W + \xi)$ where ξ is a random number uniformly distributed on the unit interval $0 < \xi < 1$, push N copies of the $\vec{R}'$ walker position onto the new stack, and go back to Step 1.

This process is repeated until the old stack is empty. The approximations mentioned in Steps 2 and 3 typically consist of replacing $\Psi_T(\vec{R}')$ by a Taylor series approximation around $\vec{R}$.

Generalizing to the full expression in (23) is straightforward. It is convenient to label the terms on the right-hand side of (23) in order as term 1, term 2, and term 3.

1. Pop a walker off the old stack and select a value of U and the radii of the spheres around each particle for the domain. This is done so that $U - V(\vec{R}'') > 0$ for all $\vec{R}''$ in the domain.

2. Sample a time τ and whether a surface (term 2) or a volume (term 1 or term 3) step is taken. The probability of selecting a surface or volume step is determined by the relative norms of the three terms on the right-hand side of (23). The approximate calculation of these norms is facilitated by noting that
$$(E_T + E_C) \int d\vec{R}'' \frac{\Psi_T(\vec{R}'')}{\Psi_T(\vec{R}')} G(\vec{R}'', \vec{R}') \approx 1 \tag{26}$$
with equality if perfect importance sampling is used. This equation also indicates that a low variance results from the mutually exclusive sampling of the three terms on the right-hand side of (23).

3. If a surface step is selected, sample $\vec{R}''$ from an approximation to $[\Psi_T(\vec{R}'')/\Psi_T(\vec{R}')][-\hat{n}\cdot\nabla G_U(\vec{R}'', \vec{R}', \tau)]$ and push the appropriate number (as in Step 5, of the previous example) of copies of $\vec{R}''$ onto the old stack and go to Step 1. It is helpful in understanding this step to view the old stack as a set of walkers that need to be propagated by $(E_T + E_C)[\Psi_T(\vec{R}')/\Psi_T(\vec{R})]\, G(\vec{R}', \vec{R})$ from their current position $\vec{R}$ to a new position $\vec{R}'$. Once walkers propagating via term 2 of (23) are propagated by $[\Psi_T(\vec{R}'')/\Psi_T(\vec{R})][-\hat{n}\cdot\nabla G_U(\vec{R}'', \vec{R})]$ from $\vec{R}$ to $\vec{R}''$, they need to be propagated in an identical way as the initial walkers on the old stack and may be added to them.

4. If a volume step is selected, sample $\vec{R}''$ from an approximation to $[\Psi_T(\vec{R}')/\Psi_T(\vec{R})]\, G(\vec{R}', \vec{R}, \tau)$. It is instructive to note that both term 1 and term 3 have a similar structure. A walker at a position $\vec{R}$ is sampled at a new position labeled by either $\vec{R}''$ or $\vec{R}'$. Clearly, this is just a relabeling of the same function $[\Psi_T(\vec{R}')/\Psi_T(\vec{R})]\, G(\vec{R}', \vec{R}, \tau)$ and the sampling of a new position is the same. Again the approximate inequality of (26) is used to put term 1 and term 3 on the same footing.

5. Decide whether term 1 or term 3 is chosen. For example, take term 1 with probability$(E_T + E_C)/[E_T + E_C + U - V(\vec{R}'')]$,or else take term 3.
6. In term 1 is chosen, push the appropriate number of copies of the new walker position on the new stack and go to Step 1.
7. If term 3 is chosen, puch the appropriate number of copies of the new walker position on the old stack and go to Step 1.

The iteration terminates when the old stack is empty. The new stack contains walkers sampled from $\Psi_T(\vec{R})\, \psi^n(\vec{R})$ where n is the next iteration.

A similar algorithm can easily be developed for the method in imaginary time corresponding to (7). A record of the amount of time a walker has propagated must be kept. No other difference exists.

It should be clear that just as the short-time approximation can be easily written to be a path integral calculated using the Metropolis method, the full iteration of (18) can also be written in terms of a more general path integral calculated again with the Monte Carlo method. In this case, the standard canonical ensemble Metropolis method would be replaced by a grand canonical ensemble method where intermediate time points are inserted and removed during the Metropolis walk corresponding to the various terms in (18). The time-step error inherent in current path-integral methods could be eliminated.

4. THE FIXED-NODE APPROXIMATION

The electronic structure of atoms and molecules is solved here within the fixed-node approximation.(9,10) The rule is that the walkers may never cross a node of the trial wave function. This is equivalent to enforcing the boundary condition that $\psi \to 0$ whenever $\Psi_T < 0$. This approximation is implemented by selecting the domain of G_U such that the wave function is positive for all points within the domain. In practice, a linear approximation to $\Phi(\vec{R})$ is used to predict the distance to a node, and the domain is chosen to only let electrons move a fraction of the distance to the predicted node. Typically this fraction is $\frac{1}{2}$ or somewhat smaller. If any walkers cross the node this fraction is reduced. It would be possible to find the minimum value of $\Psi_T(\vec{R})$ within the domain, but this would require several evaluations of $\Psi_T(\vec{R})$ and its derivatives. The present method seems more efficient. The fixed-node energy is an upper bound to the true ground-state energy.(8,10)

The fixed-node method is equivalent to solving for the ground state of the Hamiltonian H_{FN} defined as

$$H_{\mathrm{FN}} = H + E_\infty[\Psi_T(\vec{R})] \tag{27}$$

where

$$\begin{aligned} E_\infty(x) &= 0 \qquad \text{if} \quad x>0 \\ &= \infty \qquad \text{if} \quad x<0 \end{aligned} \tag{28}$$

and antisymmetrizing the resulting wave function ψ_{FN}. Since a repulsive potential is being added to the Hamiltonian, the energy goes up. A more rigorous argument is given by noting the equalities

$$\frac{\langle \psi_{\mathrm{FN}} | H_{\mathrm{FN}} | \psi_{\mathrm{FN}} \rangle}{\langle \psi_{\mathrm{FN}} | \psi_{\mathrm{FN}} \rangle} = \frac{\langle \psi_{\mathrm{FN}} | H | \psi_{\mathrm{FN}} \rangle}{\langle \psi_{\mathrm{FN}} | \psi_{\mathrm{FN}} \rangle} = \frac{\langle \psi_{\mathrm{FN}} | AHA | \psi_{\mathrm{FN}} \rangle}{\langle \psi_{\mathrm{FN}} | AA | \psi_{\mathrm{FN}} \rangle} \tag{29}$$

where A is an antisymmetrizing operator. The last term in (29) clearly is an upper bound to E_0 by the variational principle.

5. RESULTS AND DISCUSSION

In Table I we give results of fixed-node GFMC calculations of LiH at its equilibrium internuclear separation using two different trial functions for the nodes. The GFMC-SCF result is with a self-consistent field trial function. The GFMC-GVB result is with a generalized valence bond trial function. In this case both of the trial-wave functions give 100% of the correlation energy within statistical uncertainties.

Table II contains results using the self-consistent field-trial function and compares GFMC results with a Morse potential fit to experiment. In Tables III and IV are results of calculations on the Be atom. In this case the near degeneracy of the 2*s* and 2*p* states deforms the nodal surface away from that obtained using single Slater 2*s* orbitals which give only 71% of the correlation energy. Slightly more complicated wave functions

Table I. The Electronic Energy and Correlation Energy of LiH at the Equilibrium Internuclear Distance (3.015 Bohr) Computed by the GFMC Method[a]

ψ_{trial}	E	σ	E_{corr}	$\%_{\mathrm{corr}}$
GFMC-SCF	−8.071	0.002	0.084	101
GFMC-GVB	−8.068	0.002	0.081	98
Expt.	−8.0705	—	0.083	100

[a] Energy in hartree.

Table II. The Electronic Energy of LiH as a Function of Internuclear Distance Computed by the GFMC Method Employing a Single Determinant Self-Consistent Field-Trial Function. A Morse Potential Fit to the Experimental Data is Also shown

R	E_{DGF}	σ	E_{Expt}
3.015	−8.071	0.002	−8.0699
3.6	−8.062	0.001	−8.0624
4.8	−8.032	0.003	−8.0320

Table III. The Electronic Energy and Correlation Energy of Be Computed by the GFMC Method[a]

ψ_{trial}	E	σ	E_{corr}	$\%_{\text{corr}}$
GFMC (single ζ)	−14.640	0.006	0.067	71
GFMC-MCSCF	−14.667	0.002	0.094	100
Exp	−14.6674	—	0.0944	100

[a] Energies in hartree.

Table IV. The Excitation Energy of the Be Atom Computed by the GFMC Method[a]

Transition	E_{DGF}	σ	E_{Expt}
$^1S \rightarrow {}^3P$	2.90	0.08	2.73
$^1S \rightarrow {}^1P$	5.42	0.08	5.28
$^3P \rightarrow {}^1P$	2.52	0.08	2.55

[a] The standard deviation (σ) refers to the largest value for either state of the transition. Energies in eV.

Table V. (a) The Experimental Electronic and Correlation Energy of the C Atom. (b) The Electronic and Correlation Energy of the C Atom by the GFMC Method.[a]

(a) Experimental results

State	E	E_{corr}
^3P	-37.8420	0.1534
^1D	-37.7955	0.1642
$^3P \rightarrow {}^1D$	1.27 eV	

(b) GFMC

State	ψ_{trial}	E	σ	E_{corr}	$\%_{\text{corr}}$
^3P	MCSCF	-37.828	0.005	0.140	91
^3P	Double ζ	-37.842	0.005	0.153	100
^1D	Double ζ	-37.799	0.007	0.167	102
$^3P \rightarrow {}^1D$	—	1.17 eV	0.24		

[a] Energies in hartree except where noted.

containing p state contributions again give 100% of the correlation energy. Table IV shows the results obtainable for excitation energies of Be. The excited states are orthogonal to the ground state by symmetry and can be easily calculated with the fixed-node approximations.

Tables V and VI give results for the more complicated systems of C and H_2O. Again 90 to 100% of the correlation energies and good results for excitation energies are possible. However, for these higher Z systems, the higher total energies lead to larger variances. In the case of H_2O the error bar us 0.015, which is quite large by chemical standards. While more

Table VI. The Electronic Energy and Correlation Energy of Water ($R_{OH} = 1.81$ Bohr, $\theta = 104.45$) Computed by the GFMC Method[a]

ψ_{trial}	E	σ	E_{corr}	$\%_{\text{corr}}$
GFMC-I	-76.238	0.040	0.170	46
GFMC-II	-76.402	0.015	0.335	91
Expt.	-76.4376	—	0.370	100

[a] I and II refer to minimal Slater and double ζ for oxygen 2p functions. Energies in hartree.

computing time would lower these errors, it would not be by a large factor. With present techniques the GFMC method is limited to doing atoms and molecules with about 10 or fewer electrons.

6. CONCLUSION

We have outlined the GFMC method for atoms and molecules within the fixed-node approximation. The method used has no time-step error and therefore does not require an expensive extrapolation to zero time step. Also there is no systematic error introduced by using an approximation that is not valid even in the limit of zero time step. For example, the short-time Green's function given by

$$G_{\mathrm{ST}}(\vec{R}', \vec{R}, \Delta\tau) = (2\pi\Delta\tau)^{-3N/2} \exp\left\{ -\frac{[\vec{R}' - R - \nabla \ln \Psi_T(\vec{R})\,\Delta\tau]^2}{2\Delta\tau} - V(\vec{R})\Delta\tau \right\} \tag{30}$$

which is commonly used is not correct in this limit as a simple substitution into the equation

$$[H + (\partial/\partial\tau)]\, G_{\mathrm{ST}}(\vec{R}', \vec{R}, \Delta\tau) = 0 \tag{31}$$

and keeping terms of the same order as the potential, will demonstrate.

The GFMC method has difficulty for more than about 10 electrons. Energy differencing schemes seem to be required and are being actively sought. The fermion problem is not at present the main bottleneck to the solution of atoms and molecules. The fixed-node solutions are adequate if improved statistical accuracies can be obtained.

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