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# The Statistical Error of Green's Function Monte Carlo

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The statistical error in the ground state energy as calculated by Green's Function Monte Carlo (GFMC) is analyzed and a simple approximate formula is derived which relates the error to the number of steps of the random walk, the variational energy of the trial function, and the time step of the random walk. Using this formula it is argued that as the thermodynamic limit is approached with $N$ identical molecules, the computer time needed to reach a given error per molecule increases as $N^b$ where $0.5 < b < 1.5$ and as the nuclear charge $Z$ of a system is increased the computer time necessary to reach a given error grows as $Z^{5.5}$. Thus GFMC simulations will be most useful for calculating the properties of low $Z$ elements. The implications for choosing the optimal trial function from a series of trial functions is also discussed.

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**KEY WORDS:** Quantum Monte Carlo; simulations; variance reduction; ground state energy.

## 1. INTRODUCTION

As other contributions to the Metropolis symposium can attest, quantum Monte Carlo methods are having a large impact on many areas of physics but they are still very much in the development phase. This contribution will be concerned only with Green's Function Monte Carlo (GFMC), a method for determining ground state properties of many-body quantum systems which is based on an old idea, attributed orginally to Fermi$^{(1)}$ of regarding the Schröedinger equation in imaginary time as a diffusion and branching process. After some preliminary research on quantum Monte Carlo in the early 1950's, very little progress was made until Kalos$^{(2)}$

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applied some of the techniques from neutron transport Monte Carlo: importance sampling and iterated Green's functions. The first major application of the method, which is now called Green's Function Monte Carlo (GFMC), was by Kalos, Levesque, and Verlet(3) who calculated the exact ground state energy of approximately 100 hard spheres at densities near melting. This was followed by extensive simulations of zero temperature helium(4) which were in very good agreement with experiment. The GFMC method was then generalized to treat fermion systems.(5) These techniques go by the names of the fixed-node, release-node, and transient estimate methods and have been used to study the electron gas,(5) liquid $^3$He,(6) molecular and metallic hydrogen,(7) and molecules consisting of low $Z$ elements.(8,9)

This article does not discuss the technical details of the construction of a GFMC program, nor does it discuss any of the results obtained with this method. Rather it focuses on the statistical error of the energy as computed by the GFMC method. After an approximate formula has been derived, it will then be possible to estimate how many random walk steps will be needed to reach a prescribed accuracy for a given system, assuming that the accuracy of the importance functions is known. Thus, one may be able to determine in advance what sort of problems are amenable to GFMC calculations, something which before could only be determined after the fact. This will also give us an opportunity to explain some of the possible improvements to GFMC which could allow it to be used for a wider class of problems.

## 2. GREEN'S FUNCTION MONTE CARLO

This section introduces the basic procedure of GFMC insofar as it is needed for the discussion of the statistical errors. The reader is referred to other papers for a detailed description of the algorithm.(9-11) Let $R$ denote a point in the $3N$-dimensional configuration space where $N$ is the number of particles, and let $H$ be the nonrelativistic Hamiltonian with $\phi$ and $E_0$ being the ground state eigenvalue and eigenfunction. The process begins with a set of points $\{R_i\}(1<i<P_1)$ sampled from some initial probability distribution $f_1(R)$. This set of points is referred to as the first generation and $P_1$ is the population of the first generation (typically 100 to 10,000 points are used). From each point $R_i$ a number $W$ (hereafter called the branching factor) of new points $R_i'$ are sampled from the Green's function, $G$, written in operator notation as

$$G(R', R) = \langle R'|\, \psi[1 + t(H - E_T)]^{-1}\, \psi^{-1}\, |R\rangle \qquad (1)$$

Here $\psi$ is the *trial function* which plays a very important role, $E_T$ is the trial energy, and $t$ is the time step. These points, $R_i'$, will be referred to as the descendants of $R_i$ and, since the Green's function $G$ is not normalized, the number of descendants of $R_i$ (i.e., the branching factor) is not always one. Thus, the population in the second generation, $P_2$, can be different from $P_1$. According to (1), the distribution of points in the second generation is a sample from the function

$$f_2(R) = \int dR'\, G(R, R')\, f_1(R') \tag{2}$$

The process of sampling the Green's function $G$ is based on the von Neumann–Ulam method(12) for solving linear systems of equations. The details depend somewhat on the Hamiltonian, and it would take us too far astray to discuss how $G$ is sampled. For Coulomb systems, with which we are primarily concerned, such a sampling of $G$ can be done rather efficiently.(11,13)

Equation (2) is iterated and the third generation is sampled from the second generation and so forth until the probability distribution of points has converged to its limiting distribution $f^*(R)$, which can easily be shown to be

$$f^*(R) = \frac{1}{Z}\psi(R)\,\phi(R) \qquad \text{where} \qquad Z = \int dR\, \psi(R)\,\phi(R) \tag{3}$$

A certain number of generations in the beginning of the run are thrown away, just as in classical simulations, since they may contain a memory of the initial distribution. Usually the number to be thrown away is judged empirically, and averages are taken over points in the remaining generations.

In the limit of small time steps, the Green's function $G$ simplifies to such an extent that one can write down the explicit method of sampling the new points. This method(5,9) is called Diffusion Monte Carlo (DMC). Let "time" (which corresponds to imaginary physical time) be defined as $T = k * t$, where $k$ is the generation number. Then $f(R, T)$ satisfies the partial differential equation(5)

$$\frac{\partial f}{\partial T}(R, T) = -[E_L - E_T]\, f + \frac{\hbar^2}{2m}\nabla^2 f - \frac{\hbar^2}{m}\vec{\nabla}[f\vec{\nabla}\log\psi] \tag{4}$$

where $E_L(R) = \psi^{-1}H\psi$ is the *local energy* of the trial function. Thus equation can be interpreted directly as a stochastic process. The evolution of $f$ is a result of the three terms on the right-hand side, namely: (a) branching with an average branching factor of $\exp\{-t[E_L(R)-E_T]\}$; (b) random diffusion with a mean squared displacement between a point and its descendants in the next generation being $t\hbar^2/m$ per coordinate; (c) drift due to the trial function with a value equal to $t\hbar^2\vec{\nabla}\log(\psi)/m$. The error analysis will apply equally to the two methods since they are closely related. DMC is simpler to program and has less branching; however, GFMC rigoursly correct, even for finite timesteps.

There are two ways of calculating the ground state energy with GFMC. The *generational estimate* of the energy is obtained by determining the value of the trial energy, $E_T$, for which the population as a function of generation is constant. If the population becomes too large, $E_T$ is made smaller; if the population diminishes, $E_T$ is increased. The *local energy estimate* $e$ of the energy is the average value of the local energy over the final distribution $f^*$. Since $H$ is hermitian, the mean value of $e$ is the ground state energy

$$\langle e\rangle = \left\langle \frac{1}{P}\sum_{j=1}^{P} E_L(R_j)\right\rangle = \frac{1}{Z}\int dR\,\phi H\psi = E_0 \tag{5}$$

where $P$ is the total number of points belonging to the equilibrated generations.

Note that, as the trial function approaches an eigenstate of $H$, the local energy will approach a constant and the statistical error will approach zero. This is the *zero variance property* of quantum Monte Carlo and it exists not only for the energy, but also for specific wave function values.(14) The growth estimator for the ground state energy also has this property but only if the Green's function $G$ is known explicitly and can be sampled directly. Usually this is not the case. Hence, our analysis will be confined to the local energy estimator.

Now if the points $R_k$ of (5) were sampled independently from $f^*$, the variance of $e$ would simply be

$$V_1 = \langle (e-E_0)^2\rangle = \frac{1}{P}\left\{\frac{1}{Z}\int dR\,\phi(H\psi)^2/\psi - E_0^2\right\} \tag{6}$$

But, in fact, the points are not sampled independently; they are correlated because the descendants of a given point are nearby. If the particle interactions are strong, as is usually the case when one resorts to a Monte Carlo calculation, the time step $t$ will be chosen small to keep the branching factors reasonable, and in that limit the mean squared displacement between a point and its descendants in the next generation is $3N\hbar^2 t/m$. Hence, points in successive generations are close together and their local energies are highly correlated. It is this correlation which we want to estimate.

First, let us briefly discuss the effect of fermi statistics on the GFMC algorithm. The fermion problem has been discussed elsewhere.(15) For the purpose of determining statistical error we will simply convert a fermion system, or indeed any excited state problem, to a ground state one by using the fixed-node method. Let us suppose that the trial function is antisymmetric and let us change the Hamiltonian by making the potential energy infinite whenever the trial function is less than or equal to zero. This makes the nodes of the ground state of this new problem equal to those of the trial function. Such a change is very easy to implement in the algorithm. One simply makes the branching factor equal to zero for those steps where the sign of the trial function changes. One can show that the energy obtained with this new potential will give an upper bound to the exact fermion energy and will equal it if the nodes of $\psi$ have been chosen to coincide with the exact nodal surfaces. In fact, it is found that, for reasonable choices of $\psi$, the energies and other expectation values are rather accurate.

One can sometimes obtain exact fermion energies by introducing negatively signed random walks. This is called the release-node or transient-estimate method(15) but is only successful if the nodes of the trial function are sufficiently close to the exact nodes. The error analysis for those methods is more complex, and in fact those methods will always have larger errors per step since the cancellation of contributions from positive and negative walks always decreases the efficiency. So our estimates, below, will reflect the best one can hope to achieve with GFMC.

## 3. THE VARIANCE OF GREEN'S FUNCTION MONTE CARLO

In any random walk method—for example, Metropolis Monte Carlo—there is serial correlation between steps of the walk. In principle, for each quantity one is calculating one needs to determine the correlations in that quantity to ensure that the random walk is long enough to get reliable answers and to determine the error bars on the final results. A simple way to calculate the error bars without explicitly determining correlation times is to divide the total random walk into a number of separate "blocks," determine the block averages for all expectation values, and to find an estimate for the error bars on the total mean from the dispersion of the block averages. If the lengths of the blocks are longer than the correlation times, the error estimates will be reliable. One can judge this by varying the number of blocks to see if the error bars change. We wish, however, to develop an a priori estimate of the error which will be useful in determining what sort of problems can be attacked with GFMC. This is not to imply that the usual method of determining errors should not be followed. In arriving at an a priori estimate, several uncontrolled approximations are made, so this estimate is not necesarily correct, while the empirical estimate is correct, with probability one, given a long enough random walk. In any case, a discrepancy between the two ways of calculating errors will perhaps give valuable information about ways of improving the trial function or the random walk procedure.

To begin, one can assume, without loss of generality, that the ground state energy is zero; this simplifies the equations. From (5) the variance of the local energy estimate about the exact ground state energy (not the sample mean) is

$$V=\frac{1}{P^2}\sum_{j,k=1}^{P}\langle E_L(R_j)\,E_L(R_k)\rangle \tag{7}$$

where we have a total of $P$ points in the "equilibrated" random walk, ordered according to generations. This equation can be rewritten as

$$V=\frac{1}{P^2}\sum_{k}\langle E_L(R_k)^2\rangle+\frac{2}{P^2}\sum_{j<k}\langle E_L(R_j)\,E_L(R_k)\rangle \tag{8}$$

The first term is recognized as $V_1$ from (6) and we will define the second term as $V_2$.

Here we make a very important assumption. Let $d(j)$ be the set of all points $k$, which are descendants, not only in the next generation but in all following ones, from the point $j$. In the second term of (8) we will ignore all correlation between the point $j$ and points $k$ not in $d(j)$. Then

$$V_2=\frac{2}{P^2}\sum_{\substack{k\in d(j)\\ j}}\langle E_L(R_j)\,E_L(R_k)\rangle \tag{9}$$

This approximation gives a lower bound to the actual variance since "cousin correlation" is being neglected, i.e., correlation between two points, both of which are derived from a third point, but neither descended from the other one. This assumption could lead to a serious underestimate of the variance. Because of branching, some points are duplicates of others and we are neglecting their correlation. Calculation of such correlation is rather difficult in general because branching comes about not only from errors in the trial function, but also from difficulties of sampling the exact Green's function $G$. In diffusion Monte Carlo, where an approximation is made for the short time Green's function, all branching comes about from inadequacies of the trial function, and it is possible that the cousin correlation could be evaluated.

In addition to the neglect of the cousin correlation, we assume that there are enough generations of the equilibrated random walk so that all *correlated* descendants of a given point $j$ are eventually sampled. End effects due to the finite length of the random walk are being dropped since they are higher order in $1/P$. Now the probability density of descendants of a point $R_0$ is simply $\sum_{m=1}^{\infty} G^m(R, R_0)$ where $G^m$ is the Green's function to the $m$th power, and $m = 1$ corresponds to descendants in the first generation, $m = 2$ to the second generation, etc. Hence

$$V_2 = \frac{2}{P} \int dR\, dR_0\, E_L(R) \left[ \sum_{m=1}^{\infty} G^m(R, R_0) \right] E_L(R_0) f^*(R_0) \tag{10}$$

To evaluate this, $G$ is expanded in the eigenfunctions of $H(|\alpha\rangle$ with eigenvalues $E_\alpha$), and the definitions of $f^*$ and $E_L$ are inserted. The ground state drops out of the summations since by assumption the Hamiltonian annhilates it.

$$V_2 = \frac{2}{PZ} \sum_{\alpha > 0} \langle \psi | H | \alpha \rangle \sum_{m=1}^{\infty} (1 + tE_\alpha)^{-m} \langle \alpha | E_L | 0 \rangle \tag{11}$$

Then the summation over the generation number, $m$, is performed and after rearrangement that over the eigenfunctions collapses to give the simple result

$$V_2 = -\frac{2}{Pt} \int dR\, E_L(R)\, \phi^2(R) \tag{12}$$

There are two types of integrals which contribute to the variance. If the time step is sufficiently large so that successive points are uncorrelated, the term which measures the fluctuations in the local energy $V_1$ dominates. In most applications the time step is quite small; thus, $V_2$, which is simply the local energy averaged over the square of the exact wave function, dominates. In both $V_1$ and $V_2$, $1/\psi$ appears. In order to ensure that these integrals exist, $\psi$ can vanish only when $\phi H \psi$ does. This will be true in the case of a fixed node calculation, but care must be taken in the release-node or transient-estimate methods.

The $V_2$ integral can be further simplified by assuming that $\psi$ is close to $\phi$. A sufficient condition is

$$|\psi(R) - \phi(R)| \ll \phi(R) \qquad \text{all } R \tag{13}$$

Then, assuming now that $\psi$ is normalized, expand $1/\psi$ in terms of $(\psi/\phi - 1)$ and to first order

$$V_2 = \frac{2}{tP} \int \psi H \phi = \frac{2}{tP} E_V \tag{14}$$

where $E_V$ is the variational energy of the trial function. Assuming the time step is small enough that $V_1$ can be neglected, a lower bound to the variance of the energy in a GFMC calculation is

$$V > 2E_V/(tP) \tag{15}$$

Although a number of approximations have been made in deriving this inequality, it has been empirically found, rather suprisingly, that (15) often holds within 20%, particularly if the trial function is reasonably accurate. The lower bound is quite accurate for the electron gas, molecular and metallic hydrogen, and small molecules composed of helium and hydrogen. Better agreement than this is not practically important since changes in programming and compliers often lead to improvements in computer times of this order. In any case, the estimate of (15) works very well to obtain an order-of-magnitude estimate of the amount of computer time needed for a given problem.

The more general expression of (11) with $V_2$ from (14) is useful for determining the optimal trial function to put into a GFMC calculation. Using the "reweighting" method$^{(10)}$ with a set of configurations derived from variational Monte Carlo parameters in the trial function are varied until the minimum value of $V_1 + V_2$ is obtained. Such trial functions often perform better than those which minimize the variational energy.

## 4. IMPROVEMENTS TO THE TRIAL FUNCTION

In the GFMC algorithm, as usually implemented, the trial function and its first and second spatial derivatives are evaluated at each step of the random walk. The question then arises as to how accurate a trial function should be used. There is a trade-off between compact trial functions which can be quickly evaluated on the computer and accurate functions which have small variational energies and hence small variance per step of the random walk. Let us assume we have a sequence of trial functions $\psi_L$ with complexity $L$ and that the computer time necessary to evaluate the trial function and its local energy is proportional to $(1 + L/L_1)$. The constant term comes from the computational work needed to advance the random walk in the limit of very compact trial functions and the linear term from the additional work needed as the complexity of the trial function increases. Further suppose that the variational energy decreases exponentially in $L$ as $E_V = \exp(-L/L_2)$. For example, Frankowski and Perkeris$^{(16)}$ have expanded the helium atom wavefunction in a polynomial in Hylleraas coordinates ($r_1 + r_2$, $r_1 - r_2$, and $r_{12}$ where $r_1$ and $r_2$ are the electron positions) with the number of terms $L$ being between 58 and 246, and find that

$L_2 \sim 20$. The ability to achieve fast exponential convergence depends on picking the expansion functions and grouping them carefully. These two assumptions and (15) imply that the amount of computer time needed to obtain a given variance will be proportional to $(1 + L/L_1)\exp(-L/L_2)$. This function has a maximum at $L = L_2 - L_1$ if $L_1$ is less than $L_2$. Otherwise it is a strictly decreasing function of $L$. For the helium atom let us assume that $L_1$ is roughly 10. (The amount of time needed to compute 10 terms in the Hylleraas expansion as well as the first and second derivatives of these terms is equal to the rest of the time needed to construct one new point in the random walk). Then the least efficient trial function has 10 terms and one should either choose $L = 1$ as the trial function or the largest $L$ value available, which in this case is 246. The computer time necessary to obtain the coefficients of such an expansion have been neglected since it is trivial for helium.

For the next simplest atom, lithium, only much cruder trial functions are available. For values of $L \langle 93$, and again assuming exponential convergence, the estimate of $L_2 = 100$ is obtained from Ref. (17). Again taking $L_1 = 10$ we find that the least efficient trial function has 90 terms, the most accurate function available. For lithium, unless more accurate functions are computed, the optimal trial function is the compact $L = 1$ function. It is reasonable to expect that this is a general feature; as the number of electrons increases, the constant $L_2$ increases, and simple series expansions are less and less useful as trial functions. Of course such asymptotic arguments are not always relevant and computations with a variety of trial functions will give valuable checks on our assumptions.

In fact, one of our assumptions is not quite correct. It is not necessary to evaluate the trial function at each step. One can take as a guiding function a very compact trial function and then evaluate the local energy with a much more accurate function, but very seldom, thus, in effect, setting to zero the $V_2$ term in the variance. The difference between the two types of trial functions is accounted for with a weight equal to their ratio. For this scheme to work it is essential that there be a large overlap between the two functions. The reader is referred to ref. (18) for a practical example.

In the case where one has a sequence of highly accurate trial functions one can ask a related question: How much computer time will be necessary for the Monte Carlo error bar to become less than the variational bound? According to the assumptions above, it will grow *exponentially* as $L\exp(L/L_2)$. Since expansion methods are polynomial in $L$, Monte Carlo is not the best method for arriving at extremely precise results. This is simply because the variational upper bound is second order in the error of the trial function, while the GFMC error bar is first order. Monte Carlo is useful because with it one can use much more realistic trial functions than one can with other rigorous numerical techniques. Use of a pair product trial function for low $Z$ elements gives over 90% of the correlation energy.(9) Such trial functions have not been used in chemistry because the integrals can only be done with Monte Carlo. After many years of research even expansions in Hylleraas coordinates have not been used for molecular systems. Molecular trial functions must be expanded in terms of Slater determinants of single particle orbitals. This expansion method, called configuration interaction, converges very slowly and is not thermodynamically correct.(19) Hence there are no variational techniques for many-electron systems that yield highly accurate results (say, more than $10^{-4}$ AU). In order to fully exploit the zero variance property of GFMC, adaptive methods must be developed where the results of the random walks themselves are used to determine new, and much more accurate, trial functions, since traditional variational methods will not be able to find such functions.

## 5. THE THERMODYNAMIC LIMIT

Let us now consider the computer time requirements of going to larger and larger systems of the same type. If the system is not near a zero temperature phase transition the variational energy will be proportional to the number of atoms, $N$. The time step, $t$, will have some dependence on the number of atoms since the branching factors $W$ must be kept reasonable. If one doubles the number of atoms while keeping the time step the same, the mean squared branching factor will double. The dependence of the time step on the number of atoms can be determined in DMC since the branching by (4) is due only to the local energy. Expanding in powers of $t$, one finds $\langle W^2 \rangle = 1 + 2t^2 \langle E_L(R)^2 \rangle + 0(t^3)$. In this limit, the mean squared branching is proportional to $V_1$. The expectation value of $E_L^2$ is a thermodynamic average and will scale as $N$. Hence in order to keep $\langle W^2 \rangle$ constant, the time step will go as $N^{-0.5}$. In GFMC the branching is much larger than in DMC, but experiments with the electron gas have shown about the same relationship between branching, the time step, and the number of particles.

A much more significant variation arises from the amount of computer time needed to perform each step of the random walk. For charged particles, the evaluation of the coulomb potential involves $N^2$ operations. However, using the FFT algorithm it is possible to evaluate the potential in $N \log(N)$ operations, though such programs have not been implemented for quantum systems. For fermion systems, the calculation of the Slater determinant in the trial function involves $N^3$ operations. Iterative methods of finding the determinant in $N^2$ operations could be employed for sufficiently large systems. Furthermore, for an insulating system, sparse matrix methods exist which will cut the number of operations further, since in those systems electrons on one atom only need to be antisymmetric to those on nearby atoms. To summarize, we will assume the computer time per step grows as $N^a$, where $1 < a < 2$.

With the above assumptions, the computer time necessary to achieve a given error bar on the *energy per atom* will grow like $N^b$ where $b = 1 + 0.5 + a - 2$, and, hence, $0.5 < b < 1.5$. This is quite a respectable growth in computer time, and is only slightly worse than the situation in classical simulations $(0 < b < 1)$ where it is now routine to compute properties of systems of several thousand particles. In fact, processors are now being built to simulate up to a million classical particles. By comparision, the largest GFMC simulations have contained 216 electrons and protons forming molecular hydrogen at zero degrees.(7) We may anticipate that GFMC calculations will soon be performed for systems of several thousand particles.

However, another set of problems requires much more precision. Suppose one wishes to calculate the band gap of hydrogen. The most elementary method involves adding and subtracting a single electron and finding the effect on the total energy. To reach the thermodynamic limit for the band gap requires that the total energy be calculated to the same accuracy as the size of the system is increased. This implies that the exponent $b$ above be increased by 2 and, thus, the computer time requirements grow as $N^b$ where $2.5 < b < 3.5$. Of course, what one needs here are special methods for calculating relative energies such as have been developed for other Monte Carlo applications. Practical and exact energy difference methods are rather difficult to devise since the insertion of a charged fermion dramatically changes the time evolution of the random walk.

## 6. HEAVY ATOMS

Finally, let us consider the computer time requirements of computing the ground state energy for an atom of charge $Z$, as $Z$ is increased. The situation here is somewhat different than in the thermodynamic limit. First, the variational energy can be roughly estimated as being proportional to the correlation energy of an atom (i.e., the Hartree–Fock energy minus the exact ground state energy). For the range of $Z < 20$, the correlation energy(20) is proportional to $Z^{1.5}$. The time step $t$ changes very significantly as $Z$ is increased since the energy of the innermost electron increases as $Z^2$. So it is reasonable to expect the time step needed to follow the orbit of the 1s electron will decrease as $Z^{-2}$ and calculations for atoms up to $Z = 10$ confirm this general behavior. Similarly, the difference between the boson and fermion energy, which controls the node crossing frequency, grows roughly as $Z^2$. The above discussion regarding the computer time per step is still applicable, but within a single atom it seems unlikely that sparse matrix techniques could be used to calculate the Slater determinant or that Fourier transform techniques could be useful in determining the potential energy. Thus, at best, we expect the computer time requirements per step to grow as $Z^2$. Putting these various factors together, the computer time necessary to reach a given absolute error in the ground state energy grows as $Z^{5.5}$. It is this strong $Z$ dependence, more than the difficulties with fermi statistics, which has prevented GFMC from being used for atoms with $Z > 10$. There is a need for methods which either drop the innermost electrons by the use of pseudopotentials or which compute relative energies in such a way that innermost electrons do not dominate the calculation.

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