Quantum Monte Carlo simulations of interacting electrons

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Abstract. A brief introduction to the Monte Carlo methods and the most common types of Quantum Monte Carlo, Variational Monte Carlo and Diffusion Monte Carlo are presented. The fermion sign problem in Diffusion Monte Carlo is outlined and a way of bypassing the fixed-node approximation is discussed.

1. The idea of Monte Carlo Methods

In general all Monte Carlo methods have in common the use of random sampling, and they are the most efficient way to integrate numerically functions in many dimensions.

The starting point for the Monte Carlo integration is the expression for the average value of a function $f$ on the interval $[a,b]$:

\[
\bar{f} = \frac{1}{(b-a)} \int_a^b f(x)dx.
\] (1)

If we reverse this relation we get the expression for the value of the integral $I$:

\[
I = \int_a^b f(x)dx = (b-a) \bar{f}.
\] (2)

This means that if we have the value of $\bar{f}$ we also have the value of $I$. The aim of Monte Carlo simulation is to estimate the value of $\bar{f}$ by random sampling of the function $f$ on interval $[a,b]$. The value of the integral $I$ can be approximated by expression

\[
I \approx (b-a) \left( \frac{1}{N_S} \sum_{i=1}^{N_S} f(x_i) \right)
\] (3)

where $x_i$ are random points uniformly distributed on $[a,b]$ and $N_s$ is the number of this points. Such a method of sampling (uniform sampling) is rather ineffective, because in many practical cases, the contributions to the integral in some regions should be sampled with bigger density, in order to obtain more accurate results in reasonable time. We can do this by use of the importance sampling method. The importance sampling is applied by introducing a Probability
Distribution Function (PDF): $\rho(x) > 0$ on $[a, b]$, $\rho(x) = 0$ outside. It is convenient to assume that this function is normalized $\int_a^b \rho(x)dx = 1$. Then we can write

$$I = \int_a^b \rho(x) \frac{f(x)}{\rho(x)} dx \approx (b - a) \left( \frac{1}{N_S} \sum_{i=1}^{N_S} \rho(x_i) \left[ \frac{f(x_i)}{\rho(x_i)} \right] \right).$$  \hspace{1cm} (4)

If the interval $[a, b]$ is sampled according to $\rho(x)$ then the above expression reduce to the final estimator of the integral

$$I \approx \frac{1}{N_S} \sum_{i=1}^{N_S} \left[ \frac{f(x_i)}{\rho(x_i)} \right].$$ \hspace{1cm} (5)

The points $x_i$ must be distributed now according to $\rho(x)$. Usually they are obtained as elements of a Markov chain generated by the Metropolis algorithm [1].

2. Quantum Monte Carlo Methods

The notion Quantum Monte Carlo denotes several different techniques based on random sampling. The simplest of these, Variational Monte Carlo (VMC), uses the Importance Sampling MC integration method to evaluate expectation values for a chosen trial wave function.

The other methods, Projector Monte Carlo are using a projection technique to obtain the ground-state component of a starting trial wave function. There are several Projector Monte Carlo methods depend on the projector operator they use, the most popular is Diffusion Monte Carlo (DMC) method, based on the imaginary time Schrodinger equation evolution operator.

Both VMC and DMC are used to calculate ground-state expectation values for correlated systems, they can also be used to specific excited states. For simulating systems at finite temperature the Path Integral Monte Carlo (PIMC) method, based on the path-integral formalism of quantum mechanics elaborated by Feyman is used. The advantage of the DMC and PIMC methods in application to fermion systems is tempered by the sign problem arising from the antisymmetry of many-fermion wave function. One of the widely used techniques to overcome this problem is so-called "fixed-node approximation" in DMC and "restricted path approximation" in PIMC. The application of DMC to fermion system and an attempt to bypass the fixed-node approximation would be presented in more details further.

Despite of the sign problem Quantum Monte Carlo QMC methods are very powerful tools for calculating the electronic properties of interacting electrons in atoms, molecules and solids. The computational cost in QMC increases as the cube of the number of particles, so it is possible to study systems containing hundreds or even several thousands of electrons. This enables to model real condensed matter with surprising precision.

The general form of the Hamiltonian of interacting electrons in some external potential field $V$ can be written as

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} V(r_i) + \sum_{1 \leq i < j}^{N} \frac{1}{|r_i - r_j|}.$$ \hspace{1cm} (6)

The potential $V$ in the case of solid systems describes the Coulomb interaction between electrons and ionic cores.

3. Variational Monte Carlo (VMC)

In VMC [2] a trial many-electron functions containing a number of adjustable parameters is chosen and expectation values are evaluated

$$E_T = \frac{\langle \Psi_T | \hat{H} | \Psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle}.$$ \hspace{1cm} (7)
The values of these parameters are determined by minimizing the trial energy \( E_T \), the ground-state energy \( E_0 \leq \min(E_T) \). In a system of \( N \) electrons the required integrals are \( 3N \) dimensional. For such problems the Monte Carlo integration is much more efficient than conventional numerical methods. In VMC as the importance sampling PDF function usually the physical density function is chosen

\[
\rho(R) = \Psi_T^*(R) \Psi_T(R)
\]

where \( R = r_1, ..., r_N \).

If we define local energy \( E_L(R) \)

\[
E_L(R) = \frac{\hat{H} \Psi_T(R)}{\Psi_T(R)}
\]

then we can write

\[
\frac{\langle \Psi_T | \hat{H} | \Psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle} = \frac{\int \rho(R) E_L(R) dR}{\int \rho(R) dR} \approx \frac{1}{NS} \sum_{i=1}^{NS} E_L(R_i)
\]

where \( R_i \) are random points in the underlying configuration space, distributed according to \( \rho(x) \). The quality of the trial function can be estimated by the local energy variance \( \sigma^2(E_L) \).

The main problem of VMC is that the accuracy of calculations depends strongly on the shape and parametrization of the trial wave function. Usually, the VMC calculations are used as a preliminary step for more advanced method DMC.

4. The form of the trial many-particle wave function

The quality of the trial wave function is crucial for the final accuracy of any VMC or DMC simulation. The time of evaluation of the trial wave function is also very essential feature. So, trial wave functions should be both accurate and easy to evaluate. QMC simulations of solids typically use trial wave functions of the Slater-Jastrow type \([3]\), consisting of a single Slater determinant multiplied by a symmetric non-negative Jastrow correlation factor.

\[
\Psi_T(x_1, ..., x_N) = \Psi_{AS}(x_1, ..., x_N) e^{-\sum_{i \leq j} u_{ss'}(|r_i - r_j|)}
\]

where \( \Psi_{AS}(x_1, ..., x_N) \) is the Slater determinant

\[
\Psi_{AS}(x_1, ..., x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(x_1) & \psi_1(x_2) & \cdots & \psi_1(x_N) \\ \psi_2(x_1) & \psi_2(x_2) & \cdots & \psi_2(x_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(x_1) & \psi_N(x_2) & \cdots & \psi_N(x_N) \end{vmatrix}
\]

and \( x_i = (r_i, \sigma_i) \), where \( \sigma_i = \pm \frac{1}{2} \) are the spin states. The orbitals \( \psi_i(x) \) in the Slater determinant are usually obtained from HF or LDA calculations. The terms \( u_{ss'}(r) \) describe the electron-electron correlations

\[
u_{ss'}(r) = \frac{A}{r} (1 - e^{-F})
\]

The correlations between pairs of electrons depend on their mutual spins orientation, so the constants \( A \) and \( F \) are spin dependent and are related by the cusp conditions

\[
\frac{du_{ss'}}{dr} \bigg|_{r=0} = \begin{cases} -\frac{1}{2} & \text{opposite spins} \\ -\frac{1}{4} & \text{parallel spins} \end{cases}
\]

Their values are adjusted by VMC calculations.
5. Diffusion Monte Carlo

DMC is a Monte Carlo method for solving of the imaginary-time Schrödinger equation

\[-\frac{\partial |\psi\rangle}{\partial \tau} = (\hat{H} - E_T) |\psi\rangle\]  

where \(\tau = it\). The formal solution of the equation can be written as

\[\psi(\mathbf{R}, \tau) = e^{-\tau(\hat{H} - E_T)}\psi(\mathbf{R}, 0)\]  

The action of the imaginary-time evolution operator on the function \(\psi(\mathbf{R}, 0)\) can be easily presented if the function is expanded in eigenstates \(\varphi_n\) of Hamiltonian \(\hat{H}\), ordered according to corresponding eigenvalues, so that \(E_n \leq E_{n+1}\),

\[\psi(\mathbf{R}, \tau) = \sum_{n=0}^{\infty} c_n e^{-\tau(E_n - E_T)} \varphi_n(\mathbf{R})\]  

\[\lim_{\tau \to \infty} \psi(\mathbf{R}, \tau) = c_0 e^{-\tau(E_0 - E_T)} \varphi_0(\mathbf{R}).\]  

It follows from (17) that in the long time limit, the imaginary-time evolution operator projects out the component corresponding to minimal energy \(E_0\). If the initial states \(\psi(\mathbf{R}, 0)\) is not orthogonal to the ground state, then the obtained state is in fact the ground-state. In order to introduce the importance sampling, we define a new function \([4, 9]\)

\[f(\mathbf{R}, \tau) = \psi_G(\mathbf{R}) \psi(\mathbf{R}, \tau),\]  

where \(\psi_G(\mathbf{R})\) is the PDF function (named "guiding" function) and is the best known approximation of the exact ground-state. Substituting (19) into (19), lead to the equation for the new function \(f(\mathbf{R}, \tau)\), which is a type of Smoluchowski-Fokker-Plank equation

\[-\frac{\partial f(\mathbf{R}, \tau)}{\partial \tau} = -\frac{1}{2} \nabla^2 f(\mathbf{R}, \tau) + \nabla \cdot [\mathbf{F}(\mathbf{R}) f(\mathbf{R}, \tau)] + (E_L(\mathbf{R}) - E_T) f(\mathbf{R}, \tau)\]  

where

\[\mathbf{F}(\mathbf{R}) = \frac{\nabla \psi_G(\mathbf{R})}{\psi_G(\mathbf{R})}\]  

is a vector in the configuration space interpreted as quantum force. To use the Monte Carlo integration, the equation (20) is transformed to the integral form \([5]\)

\[f(\mathbf{R}', \tau) = \int G(\mathbf{R} \rightarrow \mathbf{R}', \tau) f(\mathbf{R}, 0) d\mathbf{R}\]  

Introducing the short time approximation, the Green’s function \(G(\mathbf{R} \rightarrow \mathbf{R}', \tau)\) can be written as

\[G(\mathbf{R} \rightarrow \mathbf{R}', \tau) \approx e^{-\tau \left(\frac{E_L(R')}{2} + \frac{E_L(R)}{2} - E_T\right)} e^{-\frac{(R' - \mathbf{R} - \mathbf{F}(\mathbf{R}))^2}{2\tau}}\]  

\[\begin{array}{c}
\text{branching} \\
\text{diffusion}
\end{array}\]  

The two factors in (23) correspond to two processes diffusion and branching respectively. In Monte Carlo simulation the two processes are treated separately. In practice, the simulation is based on a set of walkers \(\{\mathbf{R}_m\}\) (i.e set of points in the configuration space) initially distributed according to the guiding function. During the simulation, each walker moves through the configuration space in such a way that their distribution converges to the distribution of the
ground-state. Each step of a walker splits into two stages: diffusion and branching. In the first stage a walker $R_m$ is proposed to move to a new position $R'_m$

$$R'_m = R_m + \tau F(R) + \eta$$  \hspace{1cm} (24)

where $\eta$ is a random vector in the configuration space and the move is accepted with probability

$$p_m = \min \left(1, \frac{|\psi_G(R'_m)|^2 G(R'_m \rightarrow R'_m, \tau)}{|\psi_G(R_m)|^2 G(R'_m \rightarrow R_m, \tau)} \right)$$  \hspace{1cm} (25)

according to Metropolis algorithm. In the next stage the branching process is realized, depending on the value of the branching factor

$$b_m = e^{-\frac{E_L(R'_m) + E_L(R_m) - E_T}{2}}$$  \hspace{1cm} (26)

the walker can be destroyed or new int($b_m + u$) copies of the walker created, where $u$ is a random number of $[0, 1]$. To keep the average number of workers fixed, the energy $E_T$ should be properly adjusted.

6. The fermion problem in DMC

The presented algorithm so far is exact in a sense of numerical calculation, and leads to the ground-state of the system. For electron systems, the antisymmetry of the wave function is required. This restriction is realized by applying the antisymmetry (together with all other required symmetries) to the guiding function $\psi_G(R)$. However, antisymmetric function changes sign each time when the walker crosses nodes, defined as the solution of the equation

$$\psi_G(R) = 0.$$  \hspace{1cm} (27)

This leads to the well known fermion sign problem. The most popular solution of the problem is the fixed node approximation [6, 7]. Within the method all walker moves that cross a node are rejected. In fact, each walker is confined to some region (pocket) in the configuration space. This means that within the fixed node approximation, the final state has the same nodal structure as the guiding function, so accuracy of the calculations are limited by the accuracy of the nodes of the guiding function [8]. For electrons in one-dimensional system majority of nodes are determined by electron collisions $r_i = r_j$. Collision planes are $N - 1$ dimensional and divide the configuration space into separated parts. In Figure 1 two examples of the nodal structure for four (with the same spin orientation) electrons in 1d are presented. The picture was obtained for fixed positions of two electrons. The filled circle corresponds to fixed position $(x_3, x_4)$ whereas the empty circle the transposition $(x_4, x_3)$, the collision planes are represented by the straight lines. However, if the physical space is two(three)-dimensional then the collision condition is given by two (three) equations $x_i = x_j, y_i = y_j, z_i = z_j$, so the collision planes are $2N - 2$ $(3N - 3)$ - dimensional, whereas the nodal surfaces are $2N - 1$ $(3N - 1)$ - dimensional. This means, that the nodal surfaces entirely result from the shape of the guiding function. Some nodal structures for the simplest possible case of two electrons in 2d are shown in Figure 2. The picture was obtained for fixed position $(x_2, y_2)$ one of the electrons (filled circle). It could be shown that for the linear combination of two antisymmetric functions

$$\Psi_{AS}(x_1, ..., x_N) + a \Phi_{AS}(x_1, ..., x_N)$$  \hspace{1cm} (28)

continues changing of the parameter $a$ leads to continues deformation of the nodal surfaces. In fact, the structures presented in Figure 1 were obtained for the same functions $\Psi_{AS}$ and $\Phi_{AS}$
but for different values of $a$. Assuming, that the nodal structure is much more important than the knowledge of the values of the guiding function, the technique of optimization of the guiding function based on (28) was investigated.

The guiding function $\Psi_{AS}$ (which is the best known approximation of the exact ground state of the system) was modified by the substitution

$$\Psi'(x_1, \ldots, x_N) = \Psi_{AS}(x_1, \ldots, x_N) + \sum_n a_n \Phi_{n,AS}(x_1, \ldots, x_N),$$

where $\Phi_{n,AS}$ are Slater determinants built from plane-wave functions. The coefficients $a_n$ were adjusted during simulation in VMC manner using the current states of all walkers. Additional restrictions for the coefficients resulting from the geometric symmetry of the system were fulfilled during calculations. As the operation requires transfer of a lot of data between computers in grid and is time consuming it was performed only a few dozen times during simulation.

To investigate the idea some testing calculations for the jellium model were performed. In all calculations noticeable lowering of the average total energy was observed. The typical evolution of the energy during calculating is shown in Figure 3.

7. Concluding remarks
The fixed node approximation for fermions system used in DMC calculations is the most crucial limitation of the accuracy of the calculations and requires very careful and advanced pre-
Figure 3. The local energy evolution during simulation.

calculations for guiding function. The presented here idea of dynamic changes of the nodal structure has occurred to be very promising for overcoming of the limitation. However, used in this test the linear combinations of the Slater determinants build of plane waves are very time consuming. It seems to be sensible to look for some other antisymmetric function easy to calculate and flexible in changing its nodal structure.

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References
[1] Metropolis, N., Rosenbluth, A. W., Rosenbluth, M. N., Teller, A. M., and Teller, E. 1953 J. Chem. Phys. 21 1087
[2] Umrigar, C. J., Wilson, K. G, and Wilkins, J. W. 1988 Phys. Rev. Lett. 60 1719
[3] Jastrow, R. J 1955 Phys. Rev. 98 1479
[4] Reynolds, P. J., Ceperley, D. M., Alder, B. J. and Lester, W. A. 1982 J. Chem. Phys. 77 5593
[5] Umrigar, C. J., Nightingale, M. P. and Runge, K. J. 1993 J. Chem. Phys. 99 2865
[6] Anderson, J. 1976 J. Chem. Phys. 63 130
[7] Reynolds, P. J., Ceperley, D. M., Alder, B. J., and Lester, W. A. 1982 J. Chem. Phys. 77 5593
[8] Ceperley, D. M. 1991 J. Stat. Phys. 63, 1237
[9] Foulkes, W. M. C., Mitas, L., Needs, R. J. and Rajagopal, G. 2001 Rev. of Modern Phys. 73 1