Quantum Monte Carlo Methods in Chemistry

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Contents

Abstract

We report on recent progress in the development of quantum Monte Carlo methods including variational, diffusion and path integral Monte Carlo. The basics of these methods are outlined together with descriptions of trial functions, treatment of atomic cores and remaining problems such as fixed-node errors. The recent results for atoms, molecules, clusters and extended systems are presented. The advantages, achievements and perspectives demonstrate that quantum Monte Carlo is a very promising approach for calculating properties of many-body quantum systems.

1 Introduction

This review is a brief update of the recent progress in the attempt to calculate properties of atoms and molecules by stochastic methods which go under the general name of quantum Monte Carlo (QMC). Below we will distinguish between basic variants of QMC: variational Monte Carlo (VMC), diffusion Monte Carlo (DMC), Green's function Monte Carlo (GFMC) and path integral Monte Carlo (PIMC).

The motivation for using these methods to calculate electronic structure, as opposed to methods of expanding the wave function in a basis, arises from considerations of the computational complexity of "solving" the Schrödinger equation for systems of many electrons. By the complexity we simply mean the systematic answer to the question: "How long does it take to compute some property of a system to some specified absolute error?" So the complexity is the study of the function: $T(\epsilon, \ldots)$ where T is the needed computer time and ϵ is the error. The absolute magnitude of T depends, of course, on such features as the type of computer, the compiler and the skill of the programmer which are hard to specify systematically. But the basic scaling of T with the required error, with the number of electrons and with the type of molecule should be independent of such details.

The error ϵ in this expression must be the "true" error, *i.e.* all the systematic and statistical errors. Uncontrolled approximations cannot be allowed, otherwise the complexity problem is not well-posed. Chemistry is unique in that first, there is a well tested, virtually exact theory (the Schrödinger equation) and second, the mean-field estimates of chemical energies are often surprisingly accurate. Unfortunately, *very* accurate estimates are required to provide input to real world chemistry since much of the interesting chemistry takes place at room temperature. Currently, the level of "chemical accuracy" is considered to be $\approx$ 1 kcal/mol. However, in many cases higher accuracy is necessary, *e.g.*, to calculate energy differences (say between two isomers, energy levels, or a binding energy) to better than room temperature requires an error of $\epsilon \leq$100 K $\approx$ 0.01 eV $\approx$ 0.35 mH $\approx$ 0.1 kcal/mol. Of course, there are many phenomena for which even higher accuracy is required (*e.g.,* superconductivity).

To obtain errors of 1 kcal/mol or better, it is essential to treat many-body effects accurately and, we believe, directly. Although commonly used methods such as the density functional theory within the local density approximation (LDA) or the generalized gradient approximation (GGA) may get some properties correctly, it seems unlikely that they, in general, will ever have the needed precision and robustness on a wide variety of molecules. On the other hand, methods which rely on a complete representation of the many-body wave function will take a computer time which is exponential in the number of electrons. A typical example of such an approach is the configuration interaction (CI) method which expands the wave function in Slater determinants of one-body orbitals. Each time an atom is added to the system, an additional number of molecular orbitals must be considered and the total number of determinants to reach chemical accuracy is then multiplied by this factor. Hence, an exponential dependence of the computer time on the number of atoms in the system results.

Simulation methods construct the wave function (or at positive temperature the N-body density matrix) by sampling it and therefore they do not need its value everywhere. The complexity then usually has a power-law dependence on the number of particles, $T \propto N^{\delta}$, where the exponent typically ranges from $1 \leq \delta \leq 4$, depending on the algorithm and the property. The price to be paid is that there is a statistical error which decays only as the square root of the computer time so that $T \propto \epsilon^{-2}$.

Recently, very accurate QMC calculations have been reported on few electron systems with H, He and Li atoms and on many-electron systems in the jellium model. QMC results are rapidly approaching chemical accuracy on much more complicated systems such as clusters of carbon and silicon, so the method is quickly becoming of practical importance. This progress is coming about through improvements in methods (for example, the use of pseudopotentials and fermion path integral methods), programming advances (interfacing to standard chemistry packages for building high quality trial wave functions) and advances in computer hardware (parallel computation).

We do not mean to imply that QMC has been rigorously shown to have a more favorable complexity; this is the crux of the infamous fermion sign problem of QMC that we will discuss later in this article. Rather we will argue that QMC has a number of desirable features which, even if the fermion sign problem is not solved, imply the method will still be useful:

- QMC has a favorable scaling with the size of the system with computational demands growing as $\approx N^3$.
- One can introduce thermal effects naturally, both for electrons and ions

and zero point motion for the ions.

- Besides energies, QMC can compute properties such as the optical and electric response, geometries, *etc.*

- QMC has general applicability for both isolated systems such as molecules and extended systems such as solids.

- QMC has been shown to reach chemical accuracy or beyond for small systems

Therefore, QMC has many of the ingredients of a method which can really "solve" the computational quantum many-body problem. We know of no other general methods with these characteristics. In addition, QMC and PIMC methods offer new ways of understanding chemical concepts and translating that understanding into a computationally efficient approach.

The idea of using a statistical approach for quantum many-body problems was mentioned rather early both by Wigner [1] and Fermi. Serious application began with McMillan's [2] calculation of liquid helium by the VMC method. Simultaneously, Kalos *et al.* [3, 4] had developed the GFMC methods which go beyond the variational approximation. Ceperley [5] generalized the VMC method to treat fermions in 1978 and generalized the importance sampled GFMC methods to fermion systems in 1980 [6]. Anderson introduced the fixed-node approximation to avoid the fermion sign problem in 1975 and did the first simple molecular applications[7]. The first major applications to electronic systems were performed by Ceperley and Alder on the electron gas model [6] and solid hydrogen [8]. These authors also introduced the release-node method to go beyond the fixed-node approximation for small and medium size systems [9] and applied it to systems of up to 54 electrons.

We will not exhaustively review previous applications and methods as there is a recent book on the subject [12] and reviews [13, 14] with details of methods and overviews of many applications. There are also very recent reviews by Anderson on rigorous QMC calculations for small systems [15] and on fixed-node applications [16]. The focus of this article is to examine to what extent QMC could perform calculations of chemical accuracy for larger chemical systems, to assess recent developments relevant to this quest and to point out the remaining fundamental problems. We will summarize only a few of the computational results that have been obtained, point to changes since previous review articles were written, and present our point of view as regards the future applications. We will not discuss the application of QMC methods to study vibration energies in atoms, quantum effects of nuclear motion, quantum Monte Carlo for real-time dynamics (see Ref.[10]) or to path integral calculations of single electrons in classical liquids [11].

The review is organized as follows. In the next section we briefly introduce the three main methods: VMC, DMC and PIMC. In the following section we describe the forms and optimization of trial wave functions. Then we discuss the treatment of atomic cores. Next we briefly outline selected applications to atoms, molecules, clusters and a few results for extended systems. Finally, we conclude with prospects for future progress.

2 Quantum Monte Carlo methods

Here we briefly summarize the various quantum Monte Carlo methods which have been used for calculations of electronic structure.

2.1 Variational Monte Carlo

In variational Monte Carlo (VMC) one samples, using the Metropolis rejection method, the square of an assumed trial wave function: $|\psi_T(R)|^2/\int dR|\psi_T(R)|^2$ where $R = \{\mathbf{r}_i\}$ are the coordinates of all the particles (possibly including their spin coordinates.) Using the sampled coordinates one can calculate any simple matrix element with respect to the trial wave function. In the most common example, the estimate of the variational energy is taken as an average over the sampled points:

$$E_V = \lim_{M\to\infty} \frac{1}{M} \sum_{i=1}^{M} \psi_T(R_i)^{-1} \mathcal{H} \psi_T(R_i) \tag{1}$$

where $\{R_i\}$ with $1 \le i \le M$ are points sampled from the distribution $|\psi_T(R)|^2/\int dR|\psi_T(R)|^2$. The variational energy is obtained as the average of the local energy $E_L(R) = \psi_T^{-1}(R) H \psi_T(R)$. The zero variance principle applies: as the trial function becomes more accurate the fluctuations in the local energy are reduced. The trial wave function is then chosen either: 1) to minimize the variational energy 2) to minimize the dispersion of the local energy (the variance) or 3) to maximize the overlap with the exact ground state. Any of these criteria could lead to a good trial function but there are important differences in using them in practice. The reweighting method [13, 17]is used to efficiently carry out this optimization.

VMC is a wave function based QMC method and hence is the most closely related to standard basis set approaches. In methods such as configuration interaction, based on expanding the wave function in Slater determinants, correlation appears indirectly through sums of products of one-body orbitals. However, in VMC correlation can be put into a trial wave function directly, once the problem of doing the expectation value integrals is solved. Using the pair product (Jastrow) trial function the correlation is included directly. On the other hand, one pays the price of having a statistical error from Monte Carlo integration which implies scaling of the computer time as ϵ^{-2}. Fortunately the prefactor can be reduced with good trial functions. The complexity of VMC versus the number of electrons is quite favorable as it scales as N^3, which is similar to scaling of mean-field approaches such as Hartree-Fock (HF). This enabled Ceperley [5] already in the first VMC calculations, to deal with 162 electron systems. The dominant piece for $N \to \infty$ is evaluating the determinants during the random sampling.

The difficulty with VMC is exactly identical in spirit to all the problems of traditional methods: the basis set problem. Although the wave function is vastly improved in VMC, it is difficult to know when the wave function form is sufficiently flexible and therefore it is always necessary to show that the basis set limit of a given class of trial function has been reached. Moreover, the accuracy of energy in no way implies accuracy of other properties. One can assume that many of the variational errors cancel out in going from one system to another but it is not very hard to find counterexamples. With the current class of wave functions it seems that we are far from getting chemical accuracies from VMC when applied to systems more complex than the electron gas or a single atom. In addition, in VMC one can waste a lot of time trying new forms rather than have the computer do the work. This problem is solved in a different way in the next two methods we discuss.

2.2 Diffusion Monte Carlo and Green's function Monte Carlo

DMC goes beyond VMC in that the wave function is sampled automatically during the Monte Carlo process but without an analytic form being generated. The mathematical basis of DMC is that the operator, $exp(-\tau\mathcal{H})$, acting on any initial function, will filter out the lowest energy eigenfunction of $\mathcal{H}$ from any initial state with given symmetry. Hence the following procedure is iterated until convergence is reached.

$$\phi(R, t+\tau) = \int dR' \langle R| exp\left[-\tau(\mathcal{H} - E_T)\right] |R'\rangle \phi(R', t) \tag{2}$$

where E_T is an adjustable trial energy. If we interpret the initial state as a probability distribution, this process can easily be seen to diffuse the points and cause them to branch (split or disappear). The branching originates in renormalization of the kernel in (2) which comes from the potential energy term. We already see the difficulty with the DMC method: the wave function cannot be interpreted as a probability distribution because it has both positive and negative regions for more than 2 electrons.

The simplest way around this problem is the *fixed-node* (FN) approximation introduced by Anderson [7]. Using the nodes of some good trial function we put an infinite potential barrier at those nodes. Then we can use the projection technique in one nodal region at a time (in fact, there are typically only two of them [18]) to solve for the energy and wave function. This additional potential has no effect if the nodes happen to be in the right location, otherwise it can be shown to always increase the ground state energy [19]

$$E_0 \leq E_{FN} \leq E_V \tag{3}$$

Hence we find the best wave function, consistent with an assumed set of nodes. The nodes are not exactly known except for the simplest systems. However, we can also go beyond the fixed-node approximation as will be mentioned later.

In 1974, Kalos [4] introduced the idea of importance sampling by asking the following question: What is the expected number of walkers resulting from a walker at position R_0? The answer is seen to be $\phi_0(R_0)$, the ground state wave function. With importance sampling we try to reduce the branching by putting in the best estimate of $\phi_0(R)$. Therefore we work with the distribution $f(R,t) = \psi_T(R)\phi(R,t)$ and the new Green's function: $\psi_T(R)\psi_T^{-1}(R')\langle R'|exp(-\tau\mathcal{H})|R\rangle$. With importance sampling branching is greatly reduced. A way of seeing this in detail is by taking the continuous time limit of the iteration process and writing down the evolution equation for the importance sampled distribution $f(R,t)$. Ceperley and Alder [6] showed that:

$$\frac{\partial f(R,t)}{\partial t} = \lambda \left[\sum_{i=1}^{N} \nabla_i^2 f(R,t) - \nabla_i (f(R,t) \nabla ln|\psi_T|^2) \right] - (E_L(R) - E_T) f(R,t) \tag{4}$$

where $\lambda = \hbar^2/2m$. This equation is the basis for the diffusion Monte Carlo approach. The three terms on the right-hand side correspond to diffusion, drift and branching, respectively. The branching now is with respect to the local energy and thus is under control. The details of the algorithm and its application to molecules can be found elsewhere [20]. Umrigar *et al* [21] have recently studied very carefully issues concerning the diffusion Monte Carlo method and its speed-up.

GFMC is a very similar algorithm (but developed earlier[4]) which has no time step error as it samples not only the wave function but also the Green's function itself. It is to be preferred when highly accurate results are needed and computer time requirements are not overwhelming.

We will show in the next section that, using the simplest nodes (a single Hartree-Fock determinant) gives more than 90% of the correlation energy for first row atoms and dimers (Fig.1) [22] and essentially 100% of the binding energy for dimers. One can do better by using multi-configuration nodes or even nodes from the natural orbital determinant. However, although using many Slater determinants does allow very good upper bounds, as more and more atoms are added to a system the computer time will grow exponentially quickly (to keep the same accuracy) and hence it is really a solution only for small systems.

2.3 Path integral Monte Carlo

PIMC is mathematically similar to DMC and shars many of the same advantages [24]. In fact, it goes further since a trial function is not specified and the method generates the quantum distribution directly from the Hamiltonian. We define PIMC to be a QMC method which is formulated at a positive temperature. Instead of attempting to calculate the properties of a single quantum state, we sum over all possible states, occupying them according to the Boltzmann distribution. This might sound hopeless, but Feynman's [23] imaginary time path integrals makes it almost as easy as DMC. The imaginary-time paths, instead of being open-ended as they are in DMC, close after an imaginary time $\beta = (k_B T)^{-1}$, where T is the temperature. Because of the absence of boundaries in imaginary time, it is not necessary to have a trial wave function. In DMC, the trial wave function is needed to start the paths and to predict the future outcome of a path, but if the whole world-line of a path is there it is not needed. A very important advantage of PIMC is that all observables are obtained exactly, while in DMC only energies are gotten correct. The rest have a bias caused by the importance function and removal of this bias causes additional uncertainties.

Instead of having imaginary time evolution as in DMC, one keeps the whole path in memory and moves it around. PIMC uses a sophisticated Metropolis Monte Carlo method to move the paths. One trades off the complexity of the trial function for more complex ways to move the paths[24]. One gains in this trade-off because the former changes the answer while the later only changes the computational cost.

Particle statistics come in rather differently in PIMC. A permutation operator is used to project bose and fermi symmetry. (Remember in DMC the fixed-node method with an antisymmetric trial function was used.) The permutations lead to a beautiful and computationally efficient way of understanding superfluidity for bosons, but for fermions, since one has to attach a minus sign to all odd permutations, as the temperature approaches the fermion energy a disastrous loss of computational efficiency occurs. There have been many applications of PIMC in chemistry, but almost all of them have been to problems where quantum statistics (the Pauli principle) were not important, and we will not discuss those here. The review article by Berne and Thirumalai [11] gives an overview of these applications.

Recently, there has been some progress in generalizing the path integral method to treat fermion systems which is called restricted PIMC (RPIMC) [25]. One can apply the fixed-node method also to the density matrix. The fermion density matrix is given by

$$\rho(R, R_0; t) \propto \sum_P \int_{PR_0}^{R} dR \exp\left(-\int_0^\beta dt \left[\frac{1}{4\lambda}\left[\frac{dR}{dt}\right]^2 + V(R(t))\right]\right) \quad (5)$$

where the integral (dR) is over all continuous paths starting at PR_0 and ending at R, with the restriction that

$$\rho(R(t), R_0; t) \neq 0; \qquad 0 \leq t \leq \beta. \tag{6}$$

P is a permutation of atoms with the same spin and necessarily must be even because of the restriction ($V(R)$ is the potential energy)[24]. The exact density matrix will then appear both on the l.h.s. of Eq. (5) and implicitly in the restriction on the r.h.s. of Eq. (6). This implies that there exists a restriction which does not have a fermion sign difficulty. In the fixed-node approximation, a trial density matrix is used for the restriction on the r.h.s of Eq. (6).

In the most relevant calculation to date using this method, Pierleoni *et al* [26] placed 64 electrons and 64 protons in a periodic box, and cooled it down to temperatures as low as 5000K $\approx$ 0.5 eV. At higher temperatures and pressures the expected behavior for a correlated hydrogenic plasma was recovered. But at the lowest temperature, evidence for a first order phase transition, where the electrons spontaneously went from an ionized state to a molecular H_2 state was seen. This transition had been conjectured, but the simulations have been the first strong evidence.

Although the computer time requirements were large (several months on a workstation), the human input to the calculation was much less than very similar studies with VMC and DMC (at zero temperature) [27]. RPIMC appears to be a very promising direction for constructing a black-box program for many-electron systems where correlation may be important. Also, PIMC seems to lead more easily to a physical interpretation of the results of a simulation, though very little work has yet been done on understanding the restricted paths of fermion systems. As an example, PIMC could lead to a more direct understanding of bond formation, electron pairing and localization.

There are several technical difficulties with RPIMC. The first is that the time step is smaller than 1 H^{-1}, on the order of one million degrees. Hence to work down to a temperature of 1000K takes on the order of 1000 points on the path, which is rather slow. A more serious difficulty is to come up with automatic ways of generating accurate restrictions.

3 Trial wave functions

One of the main advantages of the Monte Carlo method of integration is that one can use any computable trial function, including those going beyond the traditional sum of one-body orbital products (*i.e.*, linear combination of Slater determinants). Even the exponential ansatz of the coupled cluster (CC) method [28, 29], which includes an infinite number of terms, is not very efficient because its convergence in the basis set remains very slow. In this section we review recent progress in construction and optimization of the trial wave functions.

The trial function is very important for both the VMC and DMC methods. That one needs a good trial function in VMC is obvious. There are at least two reasons for having a good trial function in DMC. First, as mentioned earlier, the error in the nodes of the trial wave function gives rise to the fixed-node error. Secondly, it is utilized for the importance sampling which increases the efficiency of the DMC simulations substantially (typically, by more than two orders of magnitude) by decreasing the energy fluctuations resulting from sampling the local energy instead of potential energy. One can show [30] that the DMC error bar depends on the trial function as:

$$\epsilon \approx \left[\frac{2(E_V - E_0)}{\tau P}\right]^{1/2} \tag{7}$$

where τ is the timestep and P is the number of steps on the walk. Thus it is advantageous to improve the variational energy as long as that is not too costly in computer time per step.

Currently, the ubiquitous choice for the trial function is of the so-called Slater-Jastrow or pair-product form. It is a linear combination of spin-up and spin-down determinants of one-body orbitals multiplied by a correlation factor represented by an exponential of one-body, two-body, *etc* terms [17, 31]:

$$\Psi_T(R) = \sum_n d_n Det_n^{\uparrow}\left[\{\phi_\alpha(\mathbf{r}_i)\}\right] Det_n^{\downarrow}\left[\{\phi_\beta(\mathbf{r}_j)\}\right] \exp\left[U_1 + U_2 + U_3 + ...\right] \tag{8}$$

The sum of determinants in (8) can accommodate multi-configuration wave functions which are especially important in systems with a near-degeneracy features. Perhaps the simplest manifestation of this is in the Be atom [17, 21] where inclusion of an additional configuration has a very significant impact on the final energies.

The terms in the correlation factor can be formally expressed as

$$U_1 = \sum_i u_0(\mathbf{r}_i) \tag{9}$$

$$U_2 = \sum_{i<j} u_{ee}(\mathbf{r}_i, \mathbf{r}_j) + \sum_{i,I} u_{eI}(\mathbf{r}_i, \mathbf{r}_I) \tag{10}$$

$$U_3 = \sum_{i<j<k} u_{eee}(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + \sum_{i<j,I} u_{eeI}(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_I) + \sum_{i,I<J} u_{eII}(\mathbf{r}_i, \mathbf{r}_J, \mathbf{r}_I) \tag{11}$$

etc (small index letters denote electrons and capitals correspond to ions).

One of the important features of the Slater-Jastrow form is that it can describe the electron-electron cusp in the wave function directly and efficiently. The cusp is an important non-analytic feature of the true wave function whenever any two charged particles approach each other. The electron-electron cusp region gives rise to the so-called dynamical correlation. Because electrons repel each other by introducing the cusp term the electronic density is spread from high density to low-density regions [9, 32]. To get the density "back" to the optimal one, which is usually rather close to the mean-field density, it is necessary either to reoptimize the orbitals (which can be rather difficult) or to optimize the one-body term simultaneously with the electron-electron and higher order terms. Therefore the one-body term U_1 is retained in the correlation factor, although formally it can be absorbed into the orbitals.

One can also include the leading terms of three-particle non-analytic points with logarithmic terms from the Fock expansion, but their impact on the variational energy is small [21].

Several forms for the correlation terms have been proposed and tested. For example, Umrigar *et al* [17] used a Padé form of polynomials in linear combination of electron-electron (r_{ij}) and electron-ion (r_i) distances,

$$U_2 + U_3 = \sum_{i,j,I} \frac{P(r_{iI}, r_{jI}, r_{ij})}{1 + Q(r_{iI}, r_{jI}, r_{ij})} \tag{12}$$

which was then further refined [21]. Schmidt and Moskowitz [31] also provided an interpretation of the correlation part in terms of an "average backflow" and used products of powers of transformed distances $a(r) = r/(1+br)$

$$U_2 + U_3 = \sum_{i,j,I} \sum_{klm} c_{klm} a(r_{iI})^k a(r_{jI})^l a(r_{ij})^m \tag{13}$$

with b and $\{c_{klm}\}$ as variational parameters. Mitas [33] used a similar form but instead of higher powers he introduced a "tempering" scheme for the Padé constant which controls the steepness of the transformed distance and for the non-analytic part employed a separated exponential term [35]

$$U_2 + U_3 = -\sum_{i<j} \frac{c}{\gamma} e^{-\gamma r_{ij}} + \sum_{i,j,I} \sum_{k,l,m} c_{klm} a_k(r_{iI}) a_l(r_{jI}) b_m(r_{ij}) \tag{14}$$

where

$$a_k(r) = \left(\frac{\alpha_k r}{1+\alpha_k r}\right)^2, \quad \alpha_k = \alpha_0/2^{k-1}, \quad k > 0 \tag{15}$$

$$b_m(r) = \left(\frac{\beta_m r}{1+\beta_m r}\right)^2, \quad \beta_m = \beta_0/2^{m-1}, \quad m > 0 \tag{16}$$

with $a_0(r) = b_0(r) = 1$ while $\{c_{klm}\}$, α_0, β_0 are variational parameters. Very recently, a systematic expansion of the correlation factor (8) in polynomial invariants has been proposed by Mushinski and Nightingale [34].

These forms are good at capturing the dynamical part of the electron-electron correlation as shown in Fig. 1. Typically one obtains about 85% of the correlation energy. To obtain the same amount of the correlation with an expansion in determinants one would need a large basis set which generates an enormous number of determinants even for a rather small number of correlated electrons.

An important step for getting high quality trial function is the optimization process. One usually takes a set of configurations (Monte Carlo samples of electron positions) from previous runs and minimizes the variational energy or the fluctuations of the local energy [17]:

$$\sigma^2 = \frac{\int \Psi_T^2(R)[H\Psi_T/\Psi_T - E_V]^2 dR}{\int \Psi_T^2(R) dR} = \frac{1}{M} \sum_{i=1}^{M} [H\Psi_T(R_i)/\Psi_T(R_i) - E_V]^2 \tag{17}$$

where M is the number of configurations (for simplicity we omitted the reweighting factors). With the new trial function, new configurations are generated and the optimization process is repeated until the improvement in σ^2 becomes small.

It is also important to consider the fact that orbitals, which are generated by a one-body approach, are not necessarily optimal when the correlation is included [32, 21]. In general, the reoptimization of orbitals in the presence of correlation is an unsolved task. For small systems like atoms or small molecules one can use an expansion in some suitable basis set and reoptimize the expansion coefficients [21]. For larger systems the number of expansion coefficients grows rapidly. In addition, for larger systems the number of sampling points (M in the above equation) used for optimization must grow in order to find a stable minimum. Therefore the computational demands grow rapidly and currently make the orbital optimization very slow.

Grossman and Mitas [56] tried another approach for improving the orbitals. For small silicon molecules they replaced the Hartree-Fock orbitals by the natural orbitals which diagonalize the one-body density matrix. The correlated one-body density matrix was calculated within the multi-configuration Hartree-Fock using standard quantum chemistry approaches. Natural orbitals improved the agreement with experimental binding energies by about a factor of 2 with resulting discrepancies of 1-2%, *i.e.,* 0.05 eV/atom.

In uniform systems there has been more progress on forms of the trial function, going beyond that of Eq. (8) [57]. Translation symmetry greatly reduces the possible forms of wave functions. Recently, Y. Kwon *et al* [101] carried out calculations of the two-dimensional electron gas with wave functions including a backflow effect derived by a current conservation argument [36]. Backflow affects the nodes of the trial wave function, so by optimizing it, one can lower the fixed-node energy. The backflow trial function is given by

$$\Psi_T(R) = \sum_n d_n Det_n^{\uparrow}\left[\{\phi_\alpha(\mathbf{x}_i)\}\right] Det_n^{\downarrow}\left[\{\phi_\beta(\mathbf{x}_j)\}\right] \exp\left[U_1 + U_2 + U_3 + ...\right] \tag{18}$$

where the quasi-particle "coordinates" $\mathbf{x}_i, \mathbf{x}_j$ in the Slater determinants are given as

$$\mathbf{x}_i = \mathbf{r}_i + \sum_{k \neq i} f(r_{ik})(\mathbf{r}_i - \mathbf{r}_k) \tag{19}$$

where $f(r)$ is a variational function. The argument of the one-body orbital is a “dressed” position of the electron: it is a sum of its actual position plus a correction which depends on positions of remaining electrons. The results have shown that a significant amount of the fixed-node error (up to 90%) was recovered by using “backflow nodes” in the 2D and 3D homogenous electron gas.

Besides a speed-up in efficiency and higher accuracy, the calculations with the trial functions (8) have also brought an important insight into the nature of the electron-electron correlation: once the nodes of the wave function are sufficiently close to the exact ones, *e.g.*, by using a few configurations and/or optimized orbitals, about 85% (or more) of the correlation can be described by rather simple analytical forms (12-16) with of order 20-30 variational parameters. This is observed for all systems studied: atoms, molecules, medium size clusters, surfaces and solids - some of these included more than 200 valence electrons. In this way QMC has helped our understanding of electron-electron correlation and has demonstrated a significant gain in efficiency for describing these many-body effects.

4 Treatment of atomic cores in QMC

The core electrons pose a problem for QMC methods because the core energy is much larger than chemical energies and the relevant distance scale of core states is much smaller. It has been shown [30] that the scaling of computer time grows $\approx Z^6$ with the atomic number, Z. Obviously, all-electron calculations quickly become unfeasible (at least to reach a fixed accuracy on the energy) as Z increases.

Shown in Fig.1. ([22, 37]) is the Monte Carlo efficiency as a function of Z using GFMC and DMC. In the GFMC algorithm the statistical efficiency is seen to scale as $Z^{-9.5}$ while in DMC it scales as $Z^{-5.2}$. The GFMC method has particularly unfavorable scaling with Z as compared with DMC presumably because very small steps are taken. While all-electron calculations of Li and Be are within our stated chemical accuracy of 0.01 eV, clearly the all-electron algorithm cannot be used for heavier atoms and reach the needed accuracy. For the QMC methods to become practical for heavy atom systems one has to deal with core degrees of freedom in a different way.

The core electrons create two basic problems. The first one is that the very small size of the core region requires a different strategy for sampling the core region otherwise the time step that controls the movement of electrons will scale as Z^{-2}. Although this might be technically difficult it is not the main obstacle. One can modify the propagator [21] so that it reflects the strong localization of the core charge and thus to a large extent avoid substantial slowing down of the simulations.

Far more severe are the local energy fluctuations caused by the strong potentials and large kinetic energies in the core. Because of a rapidly changing density it is very difficult (although, perhaps, not impossible) to design a trial function which can decrease these fluctuations. Even though correlation is relatively less important in the core, on the absolute scale it is still very large. The core, because of the high density, large potentials and large kinetic energy, is always the strongest fluctuating term of the local energy.

First, we will briefly mention two methods in which the core electrons are kept, but their deleterious effects are reduced somewhat. In the "damped core" approach, introduced by Hammond *et al* [38], the efficiency was improved by dampening the core energy fluctuations. In this method, the wave function is written as a product of the core and valence determinants, and electrons in the core region are treated variationally while the valence space is treated by the DMC method. There is a smooth transition between the valence and core region by suppressing the DMC branching with a smooth cut-off function. Although the resulting energy depends, to a certain extent, on the particular choice of the cut-off, nevertheless successful calculations have been carried out for the atoms C, Si and Ge[38]. Carlson *et al*[39] tried to smooth out the core energy fluctuations by decreasing the strength of the electron-electron interaction inside the core region. The total energy was corrected for the average value of the missing interaction. Tests on Li and Li_2 led to an increase in efficiency by a factor of ≈ 6. There has been no further development of this method. Both approaches lack a systematic way of understanding the transferability of the algorithm from one chemical environment to another. The *core-retained* methods will be much slower than the *pseudopotential* methods because the computational effort of sampling energy fluctuations with Z^2 scaling remains.

Fortunately, for most valence properties the core remains practically inert and has a negligible impact on the valence properties. This fact can be used to eliminate the core electrons from the calculations and replace them with effective core Hamiltonians.

4.1 Nonlocal pseudopotentials

In LDA calculations, pseudopotentials (or effective core potentials) are almost always used to increase the efficiency of calculations, even for calculations involving hydrogen! This allows smoother wave functions which in turn reduces the number of basis functions. It has been found that transferability (the ability of a pseudo-atom to mimic a full-core atom) is governed by norm conservation [40], and pseudopotentials are constructed so that the pseudo-orbitals match the full-core orbitals outside the core.

Almost all pseudopotentials[41], including those which were used in QMC calculations, were generated by mean-field approaches (notable exception is the work of Dolg *et al* [42]). It is not obvious that pseudopotentials constructed in LDA or HF are appropriate for more exact approaches. Acioli and Ceperley [44] showed that the transferability for correlated wave functions is achieved if the sequence of one-body, two-body, *etc* ... density matrices for the pseudo-atom and the full-core atom match outside the core region. The most important effects are contained in the one-body density matrix which can be expressed as a diagonal sum of its natural orbitals. Therefore the pseudo-atom has to be constructed so that its natural orbitals (both occupied and unoccupied) match those of the full-core atom in spatial regions where atoms can overlap. Also the relevant part of the energy spectrum of the full-core and pseudo-atom should match. This idea was tested on several first row atoms [44], it was found that the natural orbitals generated with DMC were very similar to those obtained from CI calculations. Having determined the full-core natural orbitals, the next task is to find a valence-only Hamiltonian which yields the same natural orbitals and the experimentally measured atomic spectrum.

The error which is introduced by the pseudopotentials for valence properties depends on the size of valence space. One can also increase the accuracy by taking into the account the most important effect omitted in the "rigid" ion pseudopotential, namely the polarizability of the core. Polarizability, which is important for improving accuracy beyond 0.1 eV, is straightforward to introduce in DMC[43, 45].

4.2 Local pseudo-Hamiltonians

Bachelet *et al* [48], in the *pseudo-Hamiltonian* approach, proposed to replace the action of the core on the valence states by an effective single electron Hamiltonian. The most general one electron Hamiltonain which is local, spherically symmetric and Hermitian, has a local effective ionic potential and a spatially varying radial and tangential mass. Outside the atomic cores the potential becomes Coulombic and the mass becomes the usual scalar constant mass. The freedom in the effective ionic potential, the tangential and the radial mass can be used to tune the pseudo-Hamiltonian to mimic the action of the core electrons on the valence electrons. The approach has a great advantage in that the resulting valence Hamiltonian is local and all virtues of the DMC method immediately apply. For example, the fixed-node approximation gives an upper bound and release-node calculations can then converge to the exact answer.

The disadvantage of the pseudo-Hamiltonian is that one does not have very much flexibility in matching the core response to valence electrons with different angular momentum because the restrictions on the mass tensor are too severe, especially for first row and transition metal atoms *i.e.,* for the cases with strong nonlocalities. In particular, for transition metals it is not possible to use an Ar core because the first electron must always go into an s state [49]. In fact, this is of secondary importance since for accurate calculations, which are the aim of QMC, one has to include $3s$ and $3p$ states into the valence space for the $3d$ transition elements.

However, for the second row, which exhibits relatively small nonlocality effects, a good accuracy pseudo-Hamiltonians can be constructed. Reference ([48]) gives results for several atoms and dimers. New pseudo-Hamiltonian parametrizations for several elements from the first two rows were calculated very recently[50]. X.-P. Li *et al* [51] used a pseudo-Hamiltonian to carry out a DMC calculations on solid silicon, which resulted in excellent agreement with experiment for the cohesive energy. This demonstrated for the first time the feasibility of the DMC calculations on solids other than hydrogen.

4.3 Nonlocal pseudopotentials and DMC

The usual form of a valence-only Hamiltonian is:

$$H_{val} = H_{loc} + W \tag{20}$$

with the local part given by

$$H_{loc} = \sum_i \left[-\frac{1}{2}\nabla_i^2 + \sum_I v_{loc}(r_{iI}) + \frac{1}{2}\sum_{j\neq i}\frac{1}{r_{ij}} \right] \tag{21}$$

The nonlocal pseudopotential operator W includes pseudopotentials $v_\ell(r)$ for a small number of the lowest symmetry channels labeled by ℓ (usually *spd*)

$$\langle R|W|R'\rangle = \sum_{I,i}\sum_\ell \frac{2\ell+1}{4\pi} v_\ell(r_{iI}) \frac{\delta(r_{iI}-r'_{iI})}{r_{iI}r'_{iI}} P_\ell(\hat{\mathbf{r}}_{iI}\cdot\hat{\mathbf{r}}'_{iI}) \tag{22}$$

where P_ℓ is the Legendre polynomial. Therefore the valence states of different symmetry experience different potentials in the core region. The variational Monte Carlo can accommodate such Hamiltonians without major problems, and Fahy *et al* [52, 32] used nonlocal pseudopotentials for the first VMC simulations of solids.

The nonlocality, however, is a problem for the DMC simulations because the matrix element for the evolution of the imaginary-time diffusion is not necessarily positive. For realistic pseudopotentials the matrix elements are indeed negative and thus create a sign problem (even for one electron) with consequences similar to those of the fermion sign problem (see, *e.g.*, work of Bosin *et al* [50]).

In order to circumvent this problem it was proposed by Hurley and Christiansen [54] and by Hammond *et al* [55] to define a new transformed effective core potential by a projection onto a trial function

$$V_{eff}(R) = \Psi_T^{-1}(R)\int dR'\langle R|W|R'\rangle\Psi_T(R) \tag{23}$$

The new effective potential is explicitly many-body but local and depends on the trial function. We were able to show [53] that the energy H_{val}^{eff} converges quadratically to the exact energy of H_{val} as the trial function converges to the exact eigenstate. However, the DMC energy with V_{eff} will not necessarily be above the true eigenvalue of the original H_{val} and will depend on the quality of $\Psi_T(R)$. In addition, we have also pointed out [53] that the meaningful solutions of this Hamiltonian are ones where the wave function vanishes at the nodes of Ψ_T since the effective Hamiltonian will diverge at the nodes of Ψ_T. Hence we need to write the fixed-node Hamiltonian as:

$$H_{val}^{eff} = H_{loc} + V_{eff}(R) + V_\infty[\Psi_T(R)=0] \tag{24}$$

Table 1: Comparison of the Fe atom calculations with all electrons, Ne-core and Ar-core pseudopotentials.

	all-electron	Ne core	Ar core
E_{HF}	-1262.444	-123.114	-21.387
E_{VMC}	-1263.20(2)	-123.708(2)	-21.660(1)
σ^2	$\approx$ 50	1.54	0.16
$\kappa/\kappa_{\rm all}$	1	$\approx$ 0.3	$\approx$ 0.05
efficiency	0.02	2.1	125.
valence errors	0.	$\approx$ 0.1 eV	$\approx$ 0.5 eV

where the last term, which is infinite on the subspace for which $\Psi_T(R) = 0$, assures that the nodes of the solution will coincide with the nodes of $\Psi_T(R)$. A study of the projection and fixed-node errors for B, Al, Ga and In atoms has been carried out by Flad *et al* [46].

The speed-up resulting from the use of pseudopotentials can be demonstrated on the example of the iron atom [33, 58]. Table 1. gives total energies, typical values for the dispersion of the local energy, decorrelation time κ for obtaining an independent sample of energy normalized to the all electron case, and finally, the efficiency is proportional to $1/(\kappa\sigma^2)$. It is evident that with increasing size of the core the efficiency but also the systematic errors introduced by the pseudopotentials are increasing. For the given case of iron the best compromise, if we accept the accuracy level 0.1 eV, is the Ne core. This comparison gives a qualitative picture between various choices of valence space and should not be taken as a definitive one: to some extent one can always change some of these factors through improvement of the trial function, more efficient sampling and so forth.

A number of VMC and DMC calculations of atomic, molecular and solid systems have been carried out by this approach. This includes *sp* and transition element atoms [53, 33, 47], silicon and carbon clusters [56, 59], nitrogen solids [60] and diamond [61]. Our experience indicates that with sufficient number of valence electrons one can achieve a high *final* accuracy. This, however, requires using $3s$ and $3p$ in the valence space for the $3d$ elements and, possibly, $2s$ and $2p$ states for elements such as Na. Once the core is sufficiently small, the systematic error of the fixed node approximation is larger than the systematic error from pseudopotentials and their subsequent projection in the DMC algorithm. Of course, developments of better trial functions or better pseudopotentials could change these errors. The accuracy of pseudopotentials is one of the important factors which should be thoroughly tested. Rudin *et al* [62] have recently showed that commonly used pseudopotentials reproduce all electron results for the N_2 dimer with an excellent accuracy.

Interestingly, ten Haaf, van Bemmel and co-workers [63, 64] have shown that for a lattice model, it is possible to modify the effective Hamiltonian in such a way that the resulting energy is an upper bound. One can write the nonlocal operator as a sum of two pieces:

$$\langle R'|W|R\rangle = \langle R'|W_+|R\rangle + \langle R'|W_-|R\rangle \tag{25}$$

where $\langle R'|W_-|R\rangle$ are these matrix elements for which $\langle R'|W|R\rangle\Psi_T(R)\Psi_T(R') > 0$ and *vice versa* for W_+. Then it is possible to construct the following Hamiltonian

$$H_{val}^{eff*} = H_{loc} + \int dR'\langle R'|W_+|R\rangle + V_{eff-}(R) + V_\infty[\Psi_T(R) = 0] \tag{26}$$

where

$$V_{eff-}(R) = \Psi_T^{-1}(R)\int\langle R'|W_-|R\rangle\Psi_T(R')dR' \tag{27}$$

We can repeat the proof of the original paper [63] for electrons in continuous space and show that the energy of H_{val}^{eff*} will be an upper bound to the eigenvalue of H_{val}. However, the straightforward application of this will have some new features. In particular, the variance of the energy used for the DMC propagation will not go to zero even in the limit of exact trial function since W_+ is directly sampled. One can understand this from the simple example of one p electron in the field of an ion with repulsive s pseudopotential and attractive potential for all higher angular momenta (*e.g.*, the C^{3+} ion in ^2P (p^1) state). The s pseudopotential has a zero contribution to the energy of the p state since the negative and positive contributions from the projection integral exactly cancel. However, by evaluating W_- exactly while sampling W_+ in the actual Monte Carlo, we obtain zero only after averaging over many Monte Carlo samples. This means that the walkers might experience large fluctuations of energy especially in a region close to the ion where pseudopotential is large. Until such calculations are done it is not clear whether these complications will be minor for many-electron systems.

This claim can be, in fact, generalized: whenever there is a nonlocal term in the Hamiltonian then its exact sampling will produce an estimator with non-zero variance, even in the limit of the exact trial function. On the other hand, projection of the nonlocal part onto the trial function has the zero variance property, however, for a non-exact trial function the upper bound property is not guaranteed.

5 Excited states

The calculation of excited state energies has only occasionally been attempted with QMC methods. The simplest situation is to determine the excitation energy from the state of one symmetry to a state of different symmetry (*e.g.*, the 1s to 2p excitation in hydrogen). Since both states are ground states within their symmetries, one can do fixed-node calculations for each state individually and get individual upper bounds to their energies.

There are several problems with this approach. In the two separate calculations the statistical error is on the whole system while the desired energy difference (say, of the gap) is a single particle excitation. Thus a method that calculates the excitation energy directly, rather than as a difference of two independent calculations, would be preferable. In addition, the difference in energies is not bounded. If the nodes of the two states are of roughly comparable accuracy one hopes the difference will be accurate as well, but a substantial systematic error can occur, particularly since excited state trial functions are known less precisely. The final problem with this method is more serious: one would like to calculate energy difference between states with the same symmetries, *e.g.*, 1s and 2s state of the hydrogen atom. One can perform the fixed-node calculation with a 2s trial function but the result may be above or below the correct answer and the state can collapse into the 1s state. One needs to maintain orthogonality with lower states.

Ceperley and Bernu [65] introduced a method that addresses these problems. It is a generalization of the standard variational method applied to the basis set: $exp(-t\mathcal{H})\Psi_\alpha$ where Ψ_α is a basis of trial functions $1 \leq \alpha \leq m$. One performs a single diffusion Monte Carlo calculation with a guiding function which allows the diffusion to access all desired states generating a 'trajectory" $R(t)$ where t is imaginary time. With this trajectory one determines matrix elements between basis functions: $N_{\alpha,\beta}(t) =< \Psi_\alpha(t_1)|\Psi_\beta(t_1+t) >$ and their time derivatives. Using these matrix elements one can determine a sequence of upper bounds to the first m excited states. The bounds decrease exponentially fast and monotonically to the exact energies. Since the same MC data are used for all the states, some correlation of energies coming from the various states is built in. Since the bounds converge to the exact energies one has a systematic way of getting more-and-more precise energy differences by increasing t. The statistical error will also increase because of the "sign-problem", so in practice one may not be able to converge. The states are kept orthogonal, just as they are with the usual HF method.

Bernu, Ceperley and Lester [66] used this method to calculate some excited states of molecular vibrations. Kwon, Ceperley and Martin [67] used it to determine the Fermi liquid parameters in the electron gas. Correlation of walks reduced the errors in that calculation by two orders of magnitude. The method is not very stable and more work needs to be done on how to choose the guiding function and analyze the data, but it is a method that, in principle, can calculate a desired part of the spectrum from a single Monte Carlo run.

6 Exact fermion methods

Quantum Monte Carlo techniques do not yet solve rigorously the many-fermion problem because of the sign problem. To map the quantum system onto a purely probablistic process for fermions seems to require some knowledge of the wave function before we start. Solving this problem would be a major advance in computational quantum mechanics. There are a variety of claims in the literature concerning what the fermion problem is. A coherent formulation of the "fermion problem" is stated in the introduction in terms of complexity: how much computer time T will it take to compute a given property to a specified error ϵ? The error includes the effects of all the systematic and statistical errors and must be of chemical interest. The fermion simulation problem is to find a method to calculate the properties of a many-fermion system that converges as $T \propto N^\delta \epsilon^{-2}$, where δ is some small power (say, $\delta \leq 4$) and N is the number of atoms or electrons. Although there has been some work on this problem in the last few years, the solution is not in sight.

The fixed-node method does not qualify as a solution since the systematic errors are not under control, so they cannot be made arbitrarily small. There have been some recent attempts to parameterize the nodal surface and then determine the parameters dynamically. This will reduce the fixed-node errors, probably by an order of magnitude. However, it does not solve the problem since the error, even if it is smaller, is still uncontrolled. For a satisfactory solution one would have to parameterize, in a completely arbitrary fashion, the nodal surface.

In practice, there are several ways of generalizing the Slater determinant nodes. With backflow one maps the coordinates into new quasi-coordinates which then go into the orbitals of the determinant. This slows the calculation down by a factor of the number of electrons. In the second approach, one takes a sum of determinants, say, those coming from a CI calculation. The difficulty with this strategy is that as molecules get bigger, the number of possible determinants grows exponentially in the number of atoms, so this is not a viable solution to the complexity problem. What has been learned to date is that backflow works well for homogenous systems and multi-configuration wave functions for nearly degenerate systems. A systematic way of putting these together has not yet been attempted.

Two related QMC methods without systematic errors are the transient estimate and release node methods. Both of them advance the wave function with the exact (antisymmetric) fermion Green's function. They differ in that transient estimate starts from the trial function while release node starts from the fixed-node solution. Neither has the fixed-node restriction, so they introduce a minus sign weight on the random walk whenever two electrons exchange or, more correctly, whenever the walks cross the nodal surface of the trial function an odd number of times. This gives rise to an exponentially growing signal to noise ratio. The error is under control but the needed computer time is not. Suppose one chooses the number of random walks and the projection time optimally to achieve a given error. It has been shown [65] that the total error will then be related to the computer time as:

$$T \propto N^{\delta} \epsilon^{-\alpha} \tag{28}$$

where $\alpha = 2 + 2(E_F - E_B)/E_{gap}$. Here $E_F - E_B$ is the fermion ground state energy relative to the boson ground state energy and E_{gap} is the energy gap between the fermion ground state and the next highest fermion state that has some component in the trial wave function. For a boson calculation we see $\alpha = 2$; this is the usual Monte Carlo convergence. But once the fermion sign is introduced, for large N the ground state energy is extensive in the number of particles, $E = \mu N$, so that $T \propto N^{\delta} e^{-\ln(\epsilon)\mu N}$. It is no better than an explicit basis set methods such as CI.

Not to leave the reader with the impression that transient estimate and release node calculations are not useful let us briefly mention some results obtained with these methods. Already in 1980 a good convergence was obtained on the electron gas with up to 54 electrons[6]. Some of these calculations have recently been redone by Kwon [101] using better wave functions and DMC algorithms. Ceperley and Alder [9] also studied some small molecules (LiH, H_3). Recently Caffarrel and Ceperley [68] used maximum entropy methods to analyze the transient estimate energy more efficiently and rigorously, achieving the result for LiH wich agrees with experiment within 0.2 mH for the ground state energy, far better than chemical accuracy. There is no very strong reason to think that maximum entropy will change the complexity, but clearly there is room for improving the accuracy of these methods. These are valuable methods to see how good the fixed-node results are, and for local potentials they can be implemented with very little additional programming, but without future developments they will always be too slow for sufficiently large systems.

Any exact scheme where the walkers propagate independently will have the above mentioned sign problem and unfavorable complexity. To do better, one has to somehow couple the positive and negative walkers. We call a positive walker one that starts out in the positive region of Ψ_T and a negative walker one that starts out in the negative region of Ψ_T. If a positive and a negative walker approach each other, the future contribution of the pair is nearly zero so they can be cancelled out. The correct nodal surface should be established dynamically by the annihilation of pairs of walkers. This idea was originally tried out by Arnow *et al* [69]. Anderson [15] reviewed recent developments using cancellation methods including some of his own very accurate calculations on few electron systems based on the walker cancellation strategy. Bianchi *et al* have also studied the cancellation algorithms for few fermion systems [70].

Essentially the simple cancellation only works for few electron systems because the number of walkers needed to dynamically establish the nodal surface rises exponentially with the number of electrons. For stability one needs many close approaches between positive and negative walkers; one has to fill up the relevant part of phase space. Unfortunately, the size of phase space grows exponentially with the number of electrons. Some schemes reduce the size of phase space by using various symmetries such as permutation, translation, rotation or reflection symmetry [15]. Again, this helps only for small systems. Anderson estimates that the computer time needed for a stable algorithm increases by a factor of ten for each additional electron[15]. Hence the cancellation schemes so far invented do not solve the fermion problem as we have defined it in terms of complexity. Kalos, Zhang and Liu [71, 72] has recently devised a scheme which forces pairs close together thus increasing the chance for annihilation and "stabilizing" the cancellation. If this can be done sufficiently well it could change the complexity and allow for calculations on larger systems.

There has been some recent work on applying auxiliary-field techniques to continuum systems. In these techniques, the pair interaction between electrons is replaced, using the Stratonovitch-Hubbard transformation, with an interaction between electrons and a random potential, thus reducing the many-body problem to a mean-field problem. The auxiliary-field technique is extensively used for lattice models (*e.g.*, for the Hubbard model), but until recently has not been used in the continuum. One advantage of this approach is that for spin-symmetric ground states (such as the Hubbard model at half-filling) there is no fermion sign problem. However, the repulsive electron-electron interaction brings in a new sign, with difficulties similar to the ones with ordinary fermion sign. Fahy and Hamann [73], introduced the fixed-node-like method keeping only determinants with a positive projection on a Slater determinant. Zhang, Carlson and Gubernatis [74] have recently shown how to make this much more efficient with a DMC-type branching algorithm. Silvestrelli, Baroni and Car [76] have applied a similar technique (without fixed-node approximation) to an electron gas and to the H_2 molecule. They have found that it is not as efficient as DMC except in the limit of a very high density. Wilson and Gyorffy [77] recently generalized this approach to the relativistic electron gas. Until more accurate auxiliary-field techniques are developed, it is difficult to assess the prospects of these approaches for reaching the chemical accuracy.

7 Applications

7.1 Atoms and small molecules

There were many QMC calculations of the energy of atoms and small molecules. Most of these have been reviewed previously by Lester *et al* [78] and by Anderson [15, 16]. We have chosen only few of these to highlight the recent achievements.

Among the most accurate calculations by any method were QMC simulations of the H_2+H, HeH, HeHe systems by Anderson and collaborators [79, 80, 15]. The high accuracy correlated wave function with the exact Green's function algorithm which did not rely on the fixed-node approximation and had a zero time step error was used. Because the system is small one can deal with the fermion problem using a direct 'brute force' method: the low-dimensional configuration space can be filled with walkers. Using other algorithm improvements one can achieve an unprecedented precision of the final results. For example, the exact ground state of H-H-H system was estimated with error bar 0.0004 eV. In addition, a part of the energy surface for $H_2+H \rightarrow H+H_2$ reaction was evaluated together with the barrier height 9.61(1) kcal/mol. This illustrates one of the advantages of the QMC method: one can internally estimate real error bars. An earlier calculation ([9]) using GFMC with release node obtained the barrier height of 9.65 ± 0.08 kcal/mol. The difference in error bars is due to the improved trial functions and algorithms and the much greater computational resources available today. High accuracy was obtained also on other systems such as estimation of LiH total energy with 0.05 mH error bar [81].

A systematic study of the first row atoms and ions by variational Monte Carlo has been carried out by Schmidt and Moskowitz [31, 82]. These papers were important because for several reasons. First, they provided a rather simple form of the correlation factor (see Eq.(13)) based on the work of Boys and Handy [83], essentially validating their early insight. The interpretation of this correlation term as an "average backflow" also helped to understand the physical roots of the success of this form. Second, they showed that this rather simple form with a few variational parameters can recover about 70% or more of the correlation systematically through the whole first row of periodic table, as shown in Fig. 1. Third, the results also demonstrated the impact of the near-degeneracy effects which were largest for the Be atom (getting $\approx 68\%$ of the correlation) while for the Ne atom the resulting correlation was about 85% of the exact value. Further study included evaluation of the first row ionization potentials and electron affinities with very good agreement with experiment [82].

Other high accuracy all electron calculations have been carried out by Umrigar *et al* [17, 21]. Calculations of the Be atom with a two-configuration trial function and very accurate correlation factor with 109 variational parameters produced the best variational energy, with a statistical error bar of 0.03 mH and an energy higher than the estimated exact energy by only $\approx$ 0.2 mH. Calculations for the Ne atom obtained energy above the estimated ground state by $\approx$ 15 mH, which competes with the best variational result ($\approx$ 10 mH above the estimated exact energy). The latter result has been obtained by Rizzo *et al* [84] by a CI calculation which included *spdfghi* basis functions.

Another interesting calculations of Be^{2+},Ne^{8+}, Be and Ne atom have been carried out by Kenny *et al* [86] in which they evaluated perturbationally the relativistic corrections to the total energies. In particular, they found that the Breit correction is systematically larger in the Dirac-Fock approximation and calculated the most accurate values of relativistic corrections for the Ne atom to date. These results demonstrate another useful capability of the correlated wave function produced by QMC: to estimate relativistic effects. Similar study within the VMC method has been done on examples of Li and LiH [87]. We expect an important future application will be to carry out similar calculations of transition metal atoms where relativistic effects have a significant impact on the valence energy differences (*e.g.* 0.5 eV for the $s \to d$ transfer energy for the Ni atom) [88]. Only very few estimations of relativistic corrections for correlated wave functions are available for these elements[89, 90].

Other QMC capabilities have been demonstrated on the calculation of Li $2^2S \to 2^2P$ oscillator strength with significantly better agreement with experiment when compared with previous calculations [91]. Various quantities for a few electron atoms and molecules including the electric response constants were evaluated by Alexander *et al* [92]. Study of vibrational properties of molecules has been advanced by Vrbik and Rothstein for the LiH molecule using DMC estimators for the derivatives of energy with respect to the ion positions [93].

7.2 Transition metal atoms

The $3d$ transition metal atoms are rather difficult systems for traditional quantum chemistry methods and for the LDA approach. There are several complications: a very compact high-density $3d$ shell, the near-degeneracy of the $3d, 4s$ and $4p$ levels and, as we have mentioned, the relativistic effects. In addition, the $3s$ and $3p$ electrons occupy the same region of space as the $3d$ electrons and several previous calculations have shown that these states must be included into the valence space if accurate results are desired. The first QMC calculation of the correlation energy and ionization potentials for transition metals atoms Sc and Y were carried out by Christiansen [94].

Table 2 shows the QMC calculated energies of the iron atom[58] compared with LDA[95] and coupled cluster [90] calculations. These were systematic calculations of the $3d$ atom with Ne-core scalar relativistic pseudopotentials derived within the multi-configuration Hartree-Fock, and gave results very competitive or better than the CI or CC [90] calculations with an average discrepancy from experiment of ≈ 0.15 eV.

The electron affinity, which is very small for the Fe atom (0.15 eV), has so far not been reliably calculated. However, even the obtained essentially zero affinity is a tremendous improvement from the uncorrelated value of -2.36 eV. One of the reasons for the small remaining errors is that only simple trial functions were used. In particular, the determinants were constructed from Hartree-Fock orbitals. It is known that the Hartree-Fock wave function is usually more accurate for the neutral atom than for negative ion, and we conjecture that the unequal quality of the nodes could have created a bias of order of the electron affinity, especially when the valence correlation energy is more than 20 eV. One can expect more accurate calculations with improved trial functions, algorithms and pseudopotentials.

7.3 Clusters

Very recently, we were able to carry out simulations of much larger systems using nonlocal pseudopotentials. The rapid 'scale-up' shows the power of QMC to calculate properties of much large systems.

Silicon clusters provided interesting examples for testing the performance of QMC and for the study of correlation energy as a function of the size of the cluster. There are experimental data available for clusters of up to 7

Table 2: VMC and DMC first ionization potential (I. IP), electron affinity (EA) and excitation energies [eV] of the Fe atom as compared with experiment and other calculations. CCSD(T) denotes coupled cluster calculations.

	I. IP	${}^5D \to {}^3F$	${}^5D \to {}^5F$	EA
HF	6.35	7.94	2.06	-2.36
LSDA	7.93	3.04	0.10	...
CCSD(T)	7.79	...	1.07	-0.16
VMC	7.61(6)	4.73(6)	0.84(4)	-0.72(6)
DMC	7.67(6)	4.24(9)	0.84(6)	-0.03(9)
Exp.	7.87	4.07	0.87	0.15

atoms which allowed for a direct comparison. There was also a controversy between the results of LDA calculations of Röthlisberger and co-workers [96] and theoretical arguments of Phillips [97] concerning the proper treatment of correlation and structural stability of Si_{13}. Phillips argued that correlation should stabilize the icosahedral structure against a lower C_{3v} symmetry trigonal capped antiprism (Fig.4). We have carried out a systematic study of Si clusters with sizes between 2 and 20 atoms [56] to observe the structural trends. The comparison of binding energies with LDA, HF and experimental results are shown on Fig.3. The QMC results are within a few percent (0.2 eV/at.) of experimental data, decreasing the error of LDA by a factor of almost 5. These calculations also give insight into the impact of the correlation for various isomers (Fig.4): the icosahedron has indeed a larger correlation energy, but the C_{3v} ground state structure is still lower by almost 4 eV. Another remarkable fact was the observation that the correlation energy of the 20-atom cluster was very close to that found in silicon bulk crystal.

Even more interesting are carbon clusters. Raghavachari and his co-workers [98] discovered that mean-field methods have led to dramatically different results for the low-energy C_{20} isomers. The structures of these isomers are very different: a ring (D_{10h}) symmetry which is essentially a one-dimensional system, a bowl (C_{5v}) where hexagons and a pentagon lie in a slightly curved plane, and a cage (C_2) which is a distorted dodecahedron.

Table 3: Comparison of valence correlation energies (a.u.) for C_{20} in the ring, bowl, and cage geometries.

	ring	bowl	cage
CCSD(T)	-2.63	-2.70	-2.77
VMC	-2.735(3)	-2.888(4)	-2.888(4)
DMC	-3.24(1)	-3.34(1)	-3.36(1)

All these structures have closed shells with gaps ≈ 1 eV. LDA calculations predicted that the cage was the most stable structure with the bowl and ring above by 1.6 and 3.8 eV, respectively. Surprisingly, GGA (Becke-Lee-Yang-Parr functional), which is supposed to be a small correction to LDA, completely reversed this ordering. Other GGAs with different exchange-correlation functionals do not provide much more useful information: the results varied in a non-systematic way. An ambitious attempt by the CCSD(T) method with $\approx 10^7$ single and double excitations self-consistently and $\approx 10^{10}$ triples perturbatively was done by Taylor and co-workers [99]. However, a rather restricted basis set [59], which recovered about 75% of the valence correlation energy, required extrapolations that did not allow for a clear-cut prediction. The results indicated both the bowl and cage as possible lowest energy candidates. Recent QMC calculations [59] show that the correlation energy of the bowl and cage are very similar and thus the bowl is favored because of its lower electrostatic energy. The ring has a smaller correlation energy than the cage by about 3.8 eV, but with the most favorable electrostatic contribution it is placed between the bowl and cage in the overall energy ordering. This was perhaps the first time that the QMC method was used as a predictive tool for large molecular systems. The obtained correlation energies from the QMC [59] and CCSD(T) [99] methods are compared in Table 3. The computer time for the QMC calculation of a C_{20} system is about 2 hours for VMC and about 40 hours for DMC on the Cray C90 (error bar 0.01 eV/atom).

7.4 Extended systems

We will briefly mention here calculations on extended systems which have obvious relevance to chemistry and the development of QMC. Recent calculations of the 2D and 3D electron gas by Kwon *et al* [101] shed some light on the nodes of the many-body wave function by using the backflow wave function. The use of backflow modified trial functions has led to significantly lower variational energy and lower fixed-node energy, indicating that backflow modifications are important for the uniform electron gas. The improvement in the nodes was especially evident for the high density gas, while many-body terms in the correlation factor were more important for the low density case. Fahy *et al* [52, 32] first performed variational calculations of solid silicon and carbon. X.-P. Li *et al* performed the DMC calculations of solid silicon using a pseudo-Hamiltonian [51]. Fixed-node DMC calculations with local pseudopotential for solid Ge have been carried out by Rajagopal *et al*[101]. These authors have introduced also a technique to decrease the finite-size effects by using a more balanced sampling of the Brillouin zone.

There has also been some progress in expanding the solid state calculations to transition metal oxides. A VMC attempt to evaluate the cohesive energy of the NiO solid was carried out by Tanaka [102]. Although the agreement with experiment was very good, it was mainly because of a cancellation of errors as the absolute accuracy was limited by a rather simple form of trial functions. The first DMC calculations of copper oxide ($CaCuO_2$) were tested by Mitas[103] with 164 electrons in the simulation cell and Ne-core pseudopotentials on both Ca and Cu. For a nonmagnetic state the resulting cohesive energy per $CaCuO_2$ unit was 12(1) eV. The error bar is rather large because of a large total energy, but the attempt demonstrates the feasibility of such calculations and ilustrates the need for new computational strategies (parallel computing) and further method development to increase the performance. Both of these calculations are paving the way towards simulations of transition metal compounds where the accurate treatment of exchange and correlation is essential for a proper understanding of these systems.

There has been some interesting progress on the excited state calculations in insulating solid systems. Mitas and Martin [60] calculated an excited state for a solid by evaluating an exciton in a compressed nitrogen insulating solid. A similar calculation was also carried out for diamond [61]. The comparison with LDA results and experiment shows that calculations of excitons provide valuable and accurate information about the band gaps, which can be estimated from exciton energies. This technique opens new possibilities for band structure studies of insulating solids, where for excited states a proper treatment of correlation is even more important than for ground states.

An alternative method for calculating the gap has been tested by Engel *et al* [104] on a model of the 2D electron gas in a periodic potential. He estimated the gap by adding an electron to the system and evaluating the difference. The estimations were in excellent agreement with an alternative many-body method.

8 Conclusion

In this short review we have pointed out only very few of the basic issues involving the simulation of chemical systems with quantum Monte Carlo. What has been achieved in the last few years is remarkable: very precise calculations of small molecules, the most accurate calculations of the electron gas, silicon and carbon clusters, solids and simulations of hydrogen at temperatures when bonds are forming. New methods have been developed as well: high accuracy trial wave functions for atoms molecules and solids, treatment of atomic cores and the generalization of path integral Monte Carlo to treat many-electron systems at positive temperatures.

The reader may wonder why we have focused much of this review on the computational complexity. We have chosen complexity because that is the key to making these theoretical calculations an indispensable tool to scientists and engineers. It is often far from the minds of the computational scientists that "real-world" applications are much more complex than isolated molecules with a few electrons. A prototypical application is a chemical reaction of a large molecule in solution. Here, Car-Parrinello-like [105] methods have a very large impact on condensed matter chemistry and physics. They have this impact because almost any real application involves thousands if not millions of electrons. Any method which can treat the real complexity without reductionism (since that requires a highly trained theoretician) has an inherent advantage and utility. However, not only must the method be able to treat large systems, it must do so with high accuracy and reliability and must be able to calculate a whole spectrum of physical properties. For the moment that can only be done at the mean-field (LDA) level, which though often surprisingly accurate, is equally often inadequate.

The algorithms of the future will have at least three important components: accuracy, efficiency and generality. One can see that current mainstream methods fulfill at most two of these requirements. Accurate and efficient methods are not general (for example, analytical methods for low-dimensional or simplified models). Those which are general and efficient are not accurate (mean-field methods). Finally, general and accurate approaches are not efficient for large systems (such as the CI method).

It seems that QMC has all prerequisites to become the method of choice in the future as, we believe, it can fulfill all three of these requirements. Clearly, QMC's ability to scale up and treat the many-body effects directly is invaluable. But QMC also has many other attributes. For example, it is straightforward to include thermal, zero point or classical nuclear effects into PIMC. Certainly until the fermion sign problem is solved there is always a question mark hanging over the field: is the method a fundamental advance or is it merely a candidate for the most accurate approximate scheme currently known.

There are of course many opportunities and challenges for improvement of the basic methodology aside from the "sign problem." From a practical point of view, more research is needed to determine better pseudopotentials since it appears they will determine the quality of results for systems with atoms heavier than Be. What we have not discussed in depth is how important it is to compute a variety of physical relevant quantities. QMC has, for too long, been focussed on calculating the ground state energy. Path integrals are in this respect better than DMC because the trial function is eliminated and one can compute estimators directly. For that reason, they have given more insight into qualitative features such as the long range order and linear response properties. But PIMC has yet to be applied to chemically relevant systems involving many correlated electrons. Although there has been some method development, large standardized packages are not yet in existence for QMC, and as the consequence applications have been much more limited. There has been some development in the theory of how to compute spectra, forces, optimized wave functions, and geometries, but calculations of these are not yet routine. With the coming of more powerful computers and algorithms, that day is not far off.

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Fig.1. The error in the nonrelativistic total energy [mH] for the first row atoms of atomic charge Z. The upper line is from coupled cluster calculations [28]. The dashed lined with symbols and error bars denote VMC calculations [31] with a single Slater determinant and the correlation factor with 17 variational parameters. The dotted line with symbols are results of fixed-node DMC calculations with a single Slater determinant. The circles are CI calculations [85, 84].

Fig.2. The QMC efficiency as a function of atomic charge. The efficiency is defined as $1/(CPUtime\sigma^2)$. The filled squares are for GFMC calculations of the dimers (LiH, BeH ... FH) and the triangles are for GFMC calculations of the homonuclear diatomics (Li_2, B_2, .. O_2) both on the CRAY YMP [22]. It is seen that the efficiency of GFMC calculations scale as $Z^{-9.5}$. The circles are DMC calculations of Hammond [37]. The efficiency of those results scale as $Z^{-5.2}$.

Fig.3. The binding energy of silicon clusters from HF, LDA and DMC methods compared with experiment (from Ref.[56]).

Fig.4. The (negative) valence correlation energy for silicon clusters as a function of the number of atoms in the cluster. The dashed line connects the values which belong to the lowest energy structures. The filled square and circle correspond to the icosahedron and dodecahedron structures, respectively. The cross corresponds to the estimated correlation of the silicon crystal in diamond structure.