Fixed-Node Quantum Monte Carlo for Chemistry

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In this paper we discuss the application of quantum Monte Carlo (QMC) techniques to the electronic many-body problem as encountered in computational chemistry. The Fixed-Node Diffusion Monte Carlo (FN-DMC) algorithm -the most common QMC scheme for treating molecules- is presented. The impact of the fixed-node error is illustrated through numerical applications including the calculation of the electronic affinity of the chlorine atom, the dissociation barrier of the O_4 molecule, and the binding energy of the dichromium molecule, Cr_2. Although total energies calculated with FN-DMC are very accurate (more accurate than the best alternative methods available), it is emphasized that the error associated with approximate nodes can lead to important errors in the small *differences* of total energies, quantities which are particularly important in chemistry.

Keywords: Quantum Monte Carlo; Diffusion Monte Carlo; Fixed-Node approximation; Electronic structure calculations

1. Introduction

At the heart of quantitative chemistry is the formidable mathematical task consisting in finding accurate eigensolutions of the N-body electronic Schrödinger equation. This task is particularly difficult for several reasons. First, the precision required to meet the "chemical" accuracy in realistic applications is very high. For example, in the case of small organic molecules the calculation of atomization energies (the energy needed to break apart a molecule into separated atoms) requires a *relative* error on the total ground-state energies of at least 10^{-4}. Calculating electronic affinities, ionization potentials, barriers to dissociation etc. is more demanding and a level of at least 10^{-5} in accuracy is in general required. For intermolecular forces (hydrogen-bonds, van der Waals interaction, etc.) the accuracy needed is at least 10^{-6}. A second aspect which makes the electronic N-body problem difficult is the fermionic character of electrons. It is well-known that fermions are more difficult to simulate than bosons. The basic reason is that fermionic ground-states can be viewed as "mathematically" excited-states of the Hamiltonian and, therefore, display a much more intricate structure in configuration space than bosonic ground-states. Another important aspect concerns the nature of the interaction between electrons and nuclei. The existence of strong attractive nuclei centers localized at fixed positions makes the structure of the electronic distribution highly non-uniform, leading to huge density variations, a situation not easy to describe. Finally, let us emphasize that the electronic structure problem for molecules is a full N-body problem where N is large but *finite*. Many powerful tools have been developped, in particular in the condensed matter community, to treat efficiently the thermodynamical limit, $N \to \infty$. Here, we face a fully quantitative problem where the small finite variations between the N- and $(N+1)$-particle systems are of central importance.

To deal with this difficult electronic problem, a number of methods have been developped in the past sixty years. Today, two main approaches are employed. The most popular one is the Density Functional Theory (DFT). In short, DFT approaches are based on the use of approximate energy functionals of the one-body density. A major advantage of DFT is that it is computationally very efficient (computational scaling as N^3, where N is the number of electrons) and, thus, rather large electronic systems can be considered, up to several thousands of electrons. However, its main weakness is the difficulty in controlling the error made, since the choice of the most appropriate approximate energy functional to deal with a given system is a matter of physical insight and personal experience. The second approach concerns the so-called post-Hartree-Fock methods based on the use of an explicit N-body wavefunction optimized using the variational principle ("*ab initio* wavefunction-based methods"). There exist many versions of them known under various acronyms like CI (Configuration Interaction), MRCI (MultiReference CI), MPn (perturbational Möller-Plesset of order n), MCSCF (MultiConfiguration Self-Consistent Field), CASSCF (Complete Active Space SCF), CCSD(T) (Coupled Cluster with Single and Double excitations, the Triples treated perturbatively), etc. In contrast with DFT, the accuracy of the *ab initio* methods is supposed to be controlled: the larger the size of the one-particle basis set and the greater the order of the method are, the smaller the error is. However, when searching for high accuracy in large fermionic cases, in practice, the exponential increase of the size of the Fock space makes these approaches much less controlled than desired. For a large enough electronic system the size of the tractable basis set is relatively small and the quality of the know-how of the practitioner remains essential to get good results, despite the "*ab initio*" character of the approach.

The main alternative approaches to these well-established methods are the quantum Monte Carlo (QMC) techniques, a set of stochastic methods to solve the Schrödinger equation. QMC is widely used in the field of quantum solids, quantum liquids, spin systems, and nuclear matter. Successful applications include the uniform electron gas,[1] the phase diagrams of hydrogen and helium,[2] the properties of solids,[3] etc. In these various fields, QMC is considered as one of the state-of-theart methods for studying complex systems of interacting particles. In constrast, in computational quantum chemistry the situation is different. Despite a number of interesting successes (see, *e.g.*, References in[4]) QMC is still considered as a promising approach but not as an established one. The reasons for that are directly related to the various difficult aspects of the molecular many-body problem listed above, in particular to the problem of reaching a high accuracy in energy differences. In this paper we discuss one of the key difficulties -the fixed-node approximation- encountered when applying QMC to molecules.

The organization of this paper is as follows. In the first section, we present a rapid summary of the standard QMC algorithm used for electronic structure calculations, namely the Fixed-Node DMC approach. In the next section, some illustrative examples enlightening the impact of the fixed-node approximation are presented. Finally, we present some remarks summarizing the main points of the paper.

2. Fixed-Node Diffusion Monte Carlo (FN-DMC)

2.1. *The DMC algorithm*

In a quantum Monte Carlo scheme a series of "states", "configurations", or "walkers" are generated using some elementary stochastic rules. Here, a configuration is defined as the set of the $3N$-electronic coordinates (N number of electrons), the positions of the nuclei being fixed (Born-Oppenheimer approximation)

$$\vec{R} = (\vec{r_1}, ..., \vec{r_N}). \tag{1}$$

Stated differently, a configuration $\vec{R}$ may be viewed as a "snapshot" of the molecule showing the instantaneous positions of each electron. Stochastic rules are chosen so that configurations are generated according to some target probability density, $\Pi(\vec{R})$. Note that the probability density is defined over the complete $3N$-dimensional configuration space and not over the ordinary three-dimensional space. Many variants of QMC can be found in the literature (referred to with various acronyms: VMC, DMC, PDMC, GFMC, etc...). They essentially differ by the type of stochastic rules used and/or by the specific stationary density produced.

In the case of the Diffusion Monte Carlo (DMC) approach -the most popular approach for dealing with realistic systems- two basic steps are performed:

i.) a standard Monte Carlo step based on the use of a generalized Metropolis algorithm:

The walkers are moved using a Langevin-type stochastic differential equation

$$\vec{R}_{new} = \vec{R}_{old} + \vec{b}[\vec{R}_{old}]\tau + \sqrt{\tau}\vec{\eta}, \tag{2}$$

where τ is an elementary time-step, $\vec{b}$ is the so-called drift vector given by

$$\vec{b} = \frac{\vec{\nabla}\psi_T}{\psi_T}, \tag{3}$$

where ψ_T is some approximate trial wavefunction and $\vec{\eta}$ a gaussian vector made of $3N$ independent gaussian numbers with zero mean and unit variance. Each elementary move $\vec{R}_{new}$ is considered as a "trial" move and is accepted or rejected according to the acceptance probability $q \in (0,1)$ given by

$$q \equiv Min[1, \frac{\psi_T^2(\vec{R}_{new}) p(\vec{R}_{new} \rightarrow \vec{R}_{old}, \tau)}{\psi_T^2(\vec{R}_{old}) p(\vec{R}_{old} \rightarrow \vec{R}_{new}, \tau)}], \tag{4}$$

where $p(\vec{R}_{old} \rightarrow \vec{R}_{new}, \tau)$ is the transition probability density corresponding to Eq.(2), namely

$$p(\vec{R}_{old} \rightarrow \vec{R}_{new}, \tau) =$$

$$\frac{1}{(2\pi)^{3N/2}} \exp\{-[(\vec{R}_{new} - \vec{R}_{old} - \vec{b}_{old}\tau)^2]/2\tau\}. \tag{5}$$

When the move is rejected the new position of the walker is considered to be the old one. It can be easily shown that this generalized Metropolis algorithm admits ψ_T^2 as stationary density (see, *e.g.*[5]).

ii.) a branching (or birth-death) process:

Depending on the magnitude of the local energy defined as

$$E_L \equiv \frac{H\psi_T}{\psi_T}, \tag{6}$$

a given walker can be destroyed (when the local energy is greater than some estimate of the exact energy) or duplicated a certain number of times (local energy lower than the estimate of the exact energy). In practice, the branching step is very easy to implement. After each move the walker is copied a number of times equal to

$$M = Int[\exp\{-(E_L - E_T)\tau\} + u] \tag{7}$$

where $Int[]$ is the integer part of a real number, E_T some reference energy, and u an uniform random number defined over (0,1). This expression is built so that *in average* the number of copies is equal to the branching weight $\exp\{-(E_L - E_T)\tau\}$. Remark that the total number of walkers can now fluctuate and, thus, some sort of population control is required. Indeed, nothing prevents the total walker population from exploding or collapsing entirely. Various solutions to this problem have been proposed. The most popular approaches consist either in performing from time to time a random deletion/duplication step or in varying slowly enough the reference energy, E_T, to keep the average number of walkers approximately constant.

It can be shown that the stationary density resulting from these rules is given by

$$\Pi_{DMC}(\vec{R}) = \psi_T(\vec{R})\phi_0(\vec{R}) \tag{8}$$

where $\phi_0(\vec{R})$ denotes the unknown ground-state wavefunction. It is easy to verify that the exact energy is obtained as the average of the local energy over the DMC density:

$$E_0^{DMC} = \lim_{P \to +\infty} \frac{1}{P} \sum_{i=1}^{P} E_L[\vec{R}^{(i)}]. \tag{9}$$

2.2. *The Fixed-Node (FN) approximation*

For bosonic systems the ground-state does not vanish at finite distances and the DMC algorithm just described is exact within statistical uncertainties. In contrast, for fermions the algorithm is slightly biased. To understand this point we first note that the density Π_{DMC} is necessarily positive by its very definition (as any stationary density resulting from some stochastic rules). As a consequence, ϕ_0 is not the exact ground-state wavefunction but some approximate one, still solution of the Schrödinger equation but with the additional constraint that ϕ_0 has the same sign as the trial wavefunction everywhere, so that the product in Eq.(8) is always positive. Such a constraint implies that the nodes of ϕ_0 (values of $\vec{R}$ for which the wavefunction vanishes) are identical to those of the approximate wavefunction ψ_T. The resulting error is called the "fixed-node" error. Finally, it can be shown[6] that the fixed-node energy is an upper bound of the exact energy, so that FN-DMC is a truly variational method:

$$E_0^{FN-DMC} \geq E_0^{exact}. \tag{10}$$

The interested reader can find more details about the various QMC algorithms in several excellent reviews, *e.g.*[3] or.[7]

3. The accuracy of FN-DMC

3.1. *Total energies*

As a general rule, FN-DMC ground-state energies are of a very high quality. For small systems (say, number of electrons smaller than 30) the accuracy achieved is comparable or even superior to that obtained with the best high-level *ab initio* methods of computational chemistry. For larger systems, these latter approaches are just not feasible, while QMC calculations are still doable with results of similar quality. The number of electrons that can be treated by QMC is rather large. To the best of our knowledge, the largest FN-DMC all-electron calculation published so far concerns the porphyrine molecule, a system having 182 electrons.[8] Using effective core potentials to reproduce the effect of the innermost 1s electron of silicon, Williamson *et al.*[9] were able of computing the ground-state energy of a cluster of silicon and hydrogen atoms containing 986 electrons.

To give some illustrative examples we present in Table 1 several calculations performed on various atomic systems of increasing complexity: the chlorine atom (17 electrons) and its anion (18 electrons), the chromium atom (24 electrons), and the copper atom (29 electrons). All electrons (core and valence) have been included in the simulation and the FN-DMC algorithm presented above has been employed. The trial wavefunction used has a standard form consisting of a Jastrow term multiplied by a one-particle determinantal part, see *e.g.* Ref.[10] The orbitals have been chosen of the Slater type and are taken from Clementi and Roetti.[11] The time step is chosen sufficiently small to get an acceptance rate larger than 0.995.

As seen from Table 1 the ground-state energies are very good. Regarding the lighter system, the chlorine atom, the exact non-relativistic energy is known.[12] In quantum chemistry it is usual practice to measure the errors on energies as percents of the so-called correlation energy, defined as the difference of the exact non-relativistic value and the Hartree-Fock energy. For the chlorine atom the error due to the approximate Hartree-Fock nodes represents only 7% of the correlation energy. Note that this error corresponds to a relative error on the total energy (lowest eigenvalue of the Schrödinger operator) of only 0.1%. In chemistry, such a result is considered as very good.

For the Cr and Cu atoms the exact non-relativistic energies are not known. To estimate the accuracy obtained by QMC we have performed for these systems some CCSD(T) calculations using very large atomic basis sets. The CCSD(T) acronym stands for "Coupled Cluster using Single and Double excitations, the Triple excitations being treated in perturbation".[13] When the basis set is large enough and the exact wavefunction is supposed to have a strong monoconfigurational character, CCSD(T) is considered as one of the most accurate methods in computational chemistry. Very large atomic basis sets were used here; for example, in the case of the chromium and copper atoms the primitive basis set are (21s14p7d5f4g3h2i) and (22s17p11d7f5g2h2i), contracted as 244 and 270 one-particle functions, respectively. The number of derminants treated is about 6x10^8. Although CCSD(T) results are supposed to be very accurate, we see in Table 1 that FN-DMC energies are systematically better(lower).

Numerical experience on various molecular systems shows that this result is actually general. The all-electron FN-DMC method can therefore be considered as the method of choice when accurate total ground-state energies of molecular systems are searched for if the constituing atoms do not present important relativistic contributions (Z< 30).

Table 1. All-electron total ground-state energies at various levels of approximation for Cl, Cl^-, Cr, and Cu. Energies in atomic units. Statistical errors on the last digit in parentheses. HF stands for Hartree-Fock, CCSD(T) for Coupled Cluster using Simple and Double excitations, the Triple excitations being treated in perturbation, CE for Correlation Energy.

	E_{HF}	$E_{CCSD(T)}$	E_0(Fixed-Node DMC)	E_0(exact)	CE/% recovered
Cl (N_{elec}=17)	-459.4820	-459.9705	-460.1012(9)	-460.150	0.668/92.7(1)
Cl^- (N_{elec}=18)	-459.5770	-460.1046	-460.2328(24)	-460.283	0.706/92.9(3)
Cr (N_{elec}=24))	-1043.3559	-1043.8917*	-1044.310(21)	?	0.954/?
Cu (N_{elec}=29))	-1638.9632	-1640.3971	-1640.411(5)	?	1.448/?

* Averaged Coupled Pair Functional (ACPF) energy for the ^7S ground-state of Cr.

3.2. *Difference of energies*

Getting very accurate total energies is satisfactory, however, it is important to emphasize that the vast majority of chemistry problems does not require precise total energies but, rather, *accurate differences* of total energies such as barriers, enthalpies, electronic affinities, etc. A general idea valid for any approach is that accurate differences are obtained only when the systematic errors of both components nearly cancel. This is a fundamental point for any *ab initio* method and it is, of course, also true for QMC. Within the fixed-node scheme used here it means that the two following conditions need to be fulfilled. First, the statistical fluctuations are to be smaller or much smaller than the difference of energies computed. Second, the fixed-node error on both energy components must almost compensate. Thus, the quality of the results depends very much on the relative magnitudes of these two errors with respect to the desired difference. In Table 2 we present an application of FN-DMC to the computation of the electron affinity (EA) of the chlorine atom (difference of total energies between the neutral atom and its anion, Cl^-). In this example, the energy difference of the order of 10^{-1} Hartree is large for the standards of most chemical applications. For both atoms the nodes are Hartree-Fock nodes. Note that the Hartree-Fock EA has a large error (about 30%), thus illustrating the importance of electronic correlations. At the FN-DMC level, the statistical error can be easily controlled (about 2%). Within the error bars the FN-DMC result is found to coincide with the experimental result. In this example, the error related to the approximate Hartree-Fock nodes is small. Note also the fact that, in spite that the CCSD(T) energies for Cl and its anion are much less accurate than FN-DMC ones (differences of about 4 eV, see Table 1), their difference is actually very close to the difference of the latter (only 0.08 eV). This latter remark illustrates clearly the very large compensations of errors at work within the *ab initio* methods framework.

Table 2. Electron affinity (EA) of the chlorine atom in eV. Comparison between Hartree-Fock (STO basis), CCSD(T), Fixed-Node DMC, and exact or experimental results. Statistical errors on the last digit in parentheses.

	Hartree-Fock	CCSD(T)	FN-DMC	Exact or Expt
Electron Affinity	2.58	3.65	3.58(7)	3.619,3.62(Expt)

Now, most realistic situations in chemistry involve smaller energy differences. Typical cases concern energy variations of a few kcal/mol, that is $\sim 10^{-2}$ Hartree. At this level of accuracy, numerical experience shows that it is still possible to decrease enough the statistical fluctuations by using properly optimized trial wavefunctions and by performing long enough computations. However, the fixed-node error begins to play a crucial role on these small differences. In Table 3 an illustrative application involving the metastable O_4 molecule is presented. The question to solve here is to know whether or not the O_4 molecule has a sufficiently long life-time to play a role in the dynamical processes at work in the upper atmosphere.

Experimental results seem to indicate that it is indeed the case. High-level *ab initio* calculations give a slightly too low barrier. Here, the central quantity to determine is the height of the dissociation barrier for O_4 into molecular oxygen, that is the difference of total energies between the metastable O_4 singlet molecule and the two separated O_2 triplet molecules. Although there is no direct experimental value for this barrier, various dynamical models built for polyoxygen species seem to indicate that it should be greater than 10 kcal/mol. The best *ab initio* wave-function based approaches lead to a value of about 9.3 kcal/mol, a result that seems to be in contradiction with experimental findings. To elucidate this point, we have performed single reference (Hartree-Fock) and multireference FN-DMC simulations.[16] As seen in Table 3 the nature of the nodes plays a crucial role in such calculations. Using Hartree-Fock nodes, the barrier is found to be about 26 kcal/mol. Clearly, such a result is unphysical and is related to the poor quality of the Hartee-Fock nodes. Using a MCSCF (Multi-Configurational-Self-Consistent-Field) trial wave function the barrier is dramatically reduced to a value of 11.4 kcal/mol, in quantitive agreement with the experimental data.

Table 3. Dissociation barrier H of the metastable O_4 molecule in kcal/mol. Statistical errors on the last digit in parentheses.

	FN-DMC with HF nodes	FN-DMC with MCSCF nodes	*ab initio*	Expt
Barrier	H=26.2 ±2.9	H= 11.4 ±1.6	H=7.9[a],9.3[b]	H> 10

[a] CCSD(T)/aug-cc-pVDZ value from[14]
[b] CASSCF+ACPF/aug-cc-pVQZ benchmark value from[15]

Another enlightening application showing the impact of the fixed-node approximation in diffusion Monte Carlo is the calculation of the binding energy of the dichromium molecule, Cr_2. One of the most difficult problems in quantum chemistry is to accurately describe the formation and breaking of multiple bonds. In this respect, the electronic structure of the chromium dimer represents a very hard problem to describe, even though it is a “simple” diatomic molecule. The theoretical challenge arises from the fact that the dissociation of the molecular singlet ground-state leads to a couple of separate chromium atoms, each one in their S=7 spin-state (six unpaired electrons in six open shells). Accordingly, Cr_2 is considered as a genuine “bête noire” for all high-level *ab initio* correlation treatments. In Table 4 we present our all-electron FN-DMC calculations for Cr_2 at a bond length of $R = 3.2$, close to the experimental value. The trial wavefunction used Hartree-Fock nodes and the data are compared to CCSD(T) calculations and experimental ones. A first important remark is that, at the Hartree-Fock level, the Cr_2 molecule is not bound by a large amount, +0.795 a.u., although this molecule is experimentally known with a binding energy of about -0.056 a.u. This result illustrates clearly the very strong multiconfigurational character of the exact wavefunction. In quantum chemistry it is usual to split the correlation energy (defined above) into two components: a so-called dynamical correlation energy corresponding to the *instantaneous* effect of the electron-electron interaction and a static or non-dynamical correlation energy associated with a large overlap of the exact wavefunction with many mono-configurational states. Here, the proper description of the $S = 0$ wavefunction, which is expected to dissociate into two S=7 atomic states, requires to take into account in the zeroth order approximation, at least, all states (determinants) corresponding to the various ways of distributing the twelve valence electrons into the twelve valence orbitals ($4s$ and $3d$ orbitals for both atoms). The number of such states is about ~ 800000. In Table 4 we also give the binding energy obtained by Scuseria[17] using the CCSD(T) approach. As already mentioned, CCSD(T) is considered as one of the most accurate methods for computing correlation energies. However, since the method is built on a monoconfigurational reference, only the major part of the dynamical correlation energy is recovered. Using a very large basis set, Scuseria found a value of -0.018 kcal/mol. This value is very different from the experimental one and confirms the fact that, in this very complex case, the binding energy is dominated by the non-dynamic correlation energy. We have done extensive FN-DMC calculations using Hartree-Fock nodes. The basis set used is the uncontracted Partridge basis set (20s12p9d).[18] We have considered two cases corresponding to using or not f polarization functions (6f basis set functions taken from the Roos Double Zeta ANO basis[19]). As seen from the table, the effect of f functions on the FN-DMC result is important. Note that the importance of f functions in the context of HF theory has already been noticed in a previous work.[20] Now, with the largest basis set including f functions we get a FN-DMC binding energy of 0.01(3). Within statistical uncertainty this result is similar to the Scuseria's result of -0.018. It is interesting to note that, although CCSD(T) and FN-DMC are two completely different methods, similar results are obtained. In the case of the CCSD(T) method, the bad result comes from the mono-configurational character of the reference function on which the coupled cluster *ansatz* is made. In the DMC case, the origin of the large bias comes from the use of "mono-configurational" nodes.

Table 4. Total energies and binding energy of Cr_2. Bond length R=3.2 Statistical errors on the last digit in parentheses.

	FN-DMC (HF nodes, no f)	FN-DMC (HF nodes, f)	HF	CCSD(T)	Expt.
Total energies (a.u.)	-2088.522(22)	-2088.612(24)	-2085.917	-2087.516[a]	
Binding energy (a.u.)	0.10(3)	0.01(3)	0.795	-0.018	-0.056

[a] 1s core electrons not correlated in CCSD(T) (this explains why the CCSD(T) total energy is much higher than the FN-DMC one).

4. Summary

In this paper we have first summarized the various difficult aspects of the many-body problem appearing in quantum chemistry, which make this problem so difficult to solve for atomic and molecular systems. Then, we discussed the present achievments and limitations of quantum Monte Carlo techniques for this problem. After having briefly summarized the main steps of the fixed-node Diffusion Monte Carlo -the standard QMC approach in Chemistry- a number of applications have been presented. It has been illustrated that total ground-state energies obtained with FN-DMC are in general very accurate: the fixed-node error represents only a few percents of the difference between the mean-field result (Hartree-Fock) and the exact energy, the difference being called the correlation energy in quantum chemistry. For small molecules this accuracy is comparable or even superior to that of standard very high-quality *ab initio* methods traditionally used in computational chemistry (*e.g.*, Coupled Cluster with large basis sets). However, for larger molecules (let us say, with more than 50 active electrons) Fixed-Node QMC calculations are still feasible with such an accuracy, while other methods are just impossible to implement. However, it has been emphasized that in chemistry total energies are not the most relevant quantities. In general, chemists are much more interested in small differences of energies which define spectroscopic and reactivity quantities like ionization potentials, electroaffinities, reaction enthalpies and activation barriers. For these differences, we have illustrated that the fixed-node approximation can introduce sizable errors. For example, in the case of Cr_2 the DMC result using Hartree-Fock nodes predicts an unbound molecule! It is therefore important to construct physically meaningful trial wavefunctions in order to get useful FN-DMC simulations to deal with real chemistry problems.

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