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Computer Physics Communications 96 (1996) 107–117

Computer Physics
Communications

Electronic structure by quantum Monte Carlo: atoms, molecules and solids

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Received 20 March 1996

Abstract

An overview of the development, implementation and application of quantum Monte Carlo (QMC) to electronic structure calculations of real systems such as atoms, molecules and solids is presented. The relation of QMC to traditional approaches is discussed and the basic notions of variational and diffusion Monte Carlo methods are introduced. The QMC applications are illustrated on calculations of excited states of transition metal atoms, energy ordering of Si and C clusters, and cohesive energies and excitations in insulating solids. Comparisons with other methods indicate the QMC advantages in accuracy, scaling in the number of electrons and scalability on parallel architectures. The variety of treated systems demonstrates the usefulness and wide applicability of this approach. The presented results show that QMC is providing a new alternative and is becoming a powerful tool for ab initio electronic structure calculations.

1. Introduction

A number of methodologies for solving the electronic structure of real systems have been proposed over the last few decades. In spite of that, the behaviour of interacting electrons and ions described by the Schrödinger equation remains a central focal point for many physicists and chemists. The grand challenge of solving the many-body Schrödinger problem is a consequence of several key difficulties: singular Coulomb interactions, anti-symmetry and other symmetry constraints, large number of particles in a typical system of interest, and the requirement of an extremely high accuracy for meaningful results. Further complications involve, for example, zero point motion effects for systems involving light elements, relativistic effects for heavy elements, etc.

In order to simplify such a complex task, a variety of approximate approaches have been developed. The

Local Density Approximation (LDA) [1] and its further generalizations belong to the most successful approaches in this category. In the LDA approach, the estimations of the one-body electron density and ground state energy are found by minimization of an approximate energy functional derived from the theory of the homogeneous electron gas, a well-understood model system. This method continues to have a significant impact on the field of electronic structure as it often produces very reasonable results at a low computational cost. However, the LDA method is inadequate in many cases, especially when a high accuracy of the order of 0.1 eV for energy differences is required.

At the same time, many-body approaches such as Coupled Cluster (CC) or Configuration Interaction (CI) methods, based on a wavefunction expansion in an appropriate basis set [2], have been developed to a high level of sophistication [3]. However, it is well known that even if these methods are formally exact,

their applicability is limited to rather small systems because of a slow convergence in the one-particle basis set.

The development of computer technology opened new horizons for exploring stochastic strategies in quantum many-body calculations. This possibility was recognized in the early days of quantum mechanics as Fermi noted that the imaginary time Schrödinger equation represents a many-dimensional diffusion process with a branching term and with some new quantum features (anti-symmetry and other symmetry constraints). The first calculations which employed a probabilistic view on solving the Schrödinger equation were carried out by McMillan, Kalos, Ceperley and others [4,5]. These methods, known as quantum Monte Carlo (QMC), calculate samples of the many-body wavefunction and treat the many-body effects explicitly and directly. The significant advantage of QMC is that it can relatively easily capture genuine features of the many-body wavefunction such as electron–electron cusps and other multi-particle effects. On the other hand, it is much more difficult to deal efficiently with the anti-symmetry of the wavefunction in the QMC framework. Therefore QMC can be viewed as a method complementary to the traditional approaches which describe the many-body effects rather inefficiently while they maintain the antisymmetry rather easily using Slater determinants.

Our effort to build a well-founded QMC methodology, initiated several years ago [6], was focused on the following goals: development of the electronic structure QMC methods for both localized and extended systems, development of pseudopotential QMC techniques to deal with heavy atoms, implementation of the codes on vector and parallel architectures and, finally, application of these developments to real systems. In what follows, we provide a short overview of some of the important achievements of these efforts.

First, we outline the basic notions of the variational and diffusion Monte Carlo methods, forms of trial wavefunctions and treatment of atomic cores for heavy elements. Next, we present results for atoms, molecules and solids and compare the current QMC performance with other methods. Finally, some of the unsolved challenges and future tasks are discussed.

2. Methods

2.1. Variational Monte Carlo (VMC)

In variational Monte Carlo an analytically given trial wavefunction, Ψ_T , is constructed and corresponding expectation values are evaluated using stochastic integration techniques. For example, the variational energy is given by an average of the local energy E_{loc} ,

$$E_V = \frac{\langle \Psi_T | H | \Psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle} \cong \frac{1}{M} \sum_{m=1}^M \frac{H \Psi_T(R_m)}{\Psi_T(R_m)} = \frac{1}{M} \sum_{m=1}^M E_{\text{loc}}(R_m), \quad (1)$$

where H denotes the Hamiltonian of N electrons and, for simplicity, static ions,

$$H = \sum_{i=1}^N \left[-\frac{1}{2} \nabla_i^2 - \sum_l \frac{Z_l}{r_{il}} + \sum_{j>i} \frac{1}{r_{ij}} \right] + E_{\text{Ion-Ion}}, \quad (2)$$

while $\{R_m\}$ is a set of statistically independent electron configurations in $3N$ -dimensional space, distributed proportionally to $\Psi_T^2(R)$. The configurations can be generated, for example, by the Metropolis procedure [5]. The estimator has a statistical character with an error bar given by C/\sqrt{M} , where C depends on the properties of the sampled function such as its variation and smoothness but is independent of the dimensionality of the problem. The intention of statistical integration in VMC is to provide variational freedom for the functional forms of Ψ_T , discussed in more detail in Section 2.3.

Variational Monte Carlo often produces surprisingly good results. For example, VMC calculations of first row atoms with a small number of variational parameters found electron affinities and ionization potentials which are in a very good agreement with experiments [7]. For small systems with few electrons, exceedingly accurate wavefunctions and energies can be obtained [8]. Moreover, calculations of Fahy et al. [9,10] have shown that VMC combined with the elimination of atomic cores gives excellent predictions for the cohesive energies of silicon and carbon solids.

The VMC method is based on a priori given functional form(s) of Ψ_T . This is a potential source of vari-

ational bias, especially in calculations of energy differences for different systems such as isolated atoms and a solid, e.g., for the evaluation of a cohesive energy. In fact, except for a small number of cases of highly accurate calculations for few electron systems, *all* total energy methods to some extent rely on error cancellation. Arguably, this is more serious in VMC because there is much less experience with this method and also because of a lack of VMC standards.

2.2. Diffusion Monte Carlo (DMC)

The diffusion Monte Carlo method is used to eliminate a large part of the variational bias. It is based on the operator $\exp[-t(H - E)]$ which projects out the lowest state of the prescribed symmetry, Ψ , from an overlapping trial function Ψ_T ,

$$\Psi(R) \propto \lim_{t \rightarrow \infty} \Psi(R, t) = \lim_{t \rightarrow \infty} \exp[-t(H - E)] \times \Psi_T(R) \quad (\langle \Psi_T | \Psi \rangle \neq 0), \quad (3)$$

so that the function $\Psi(R, t)$ solves the imaginary time Schrödinger equation

$$-\partial_t \Psi(R, t) = (H - E) \Psi(R, t). \quad (4)$$

We can rewrite Eq. (4) into an integral form and introduce importance sampling by Ψ_T . Then the importance sampled solution $f(R, t) = \Psi(R, t) \Psi_T(R)$ obeys

$$f(R, t + \tau) = \int G(R', R, \tau) f(R', t) dR', \quad (5)$$

with the kernel

$$G(R', R, \tau) = \Psi_T^{-1}(R') \Psi_T(R) \times \langle R' | \exp[-\tau(H - E)] | R \rangle. \quad (6)$$

Formally, the stochastic solution of (5) is straightforward. The function $f(R, t)$ is represented by a set of 10^2 – 10^4 random walkers (sampling points) in the $3N$ -dimensional space of electron configurations. The walkers are propagated according to the kernel (6), which is known for small τ [5,11], and Eq. (5) is iterated to the large t limit. The propagation involves diffusion, drift and branching processes [11]. The method is formally exact provided the boundary conditions, i.e., fermion nodes where the antisymmetric solution $\Psi(R, \infty) = 0$, are known. Unfortunately, the

antisymmetry does not specify the nodes completely, and we must rely on approximations. The commonly used fixed-node approximation enforces the nodes of $f(R, t)$ to be identical to the nodes $\Psi_T(R)$. For most systems the impact of this approximation is rather small and will be illustrated on applications later.

The result of such a calculation is a set of samples of the fixed-node approximation $\Psi_D(R)$. These samples are used for estimating expectation values such as the mixed estimator E_D for the energy

$$E_D = \frac{\langle \Psi_T | H | \Psi_D \rangle}{\langle \Psi_T | \Psi_D \rangle} \cong \frac{1}{M} \sum_{m=1}^M \frac{H \Psi_T(R_m)}{\Psi_T(R_m)}, \quad (7)$$

where sampling points $\{R_m\}$ are distributed according to $f(R, t \rightarrow \infty)$. One can show that the mixed estimator is variational [12], and further details of the DMC method can be found in the book by Hammond et al. [13] and references therein.

2.3. Trial wavefunctions

The important advantage of VMC is that it enables us to build explicitly correlated wavefunctions. In addition, high accuracy wavefunctions are important also for the DMC approach because of a significant gain in efficiency. The many-body features of the true wavefunction can be incorporated into Ψ_T , and a large amount of correlation energy can be recovered using surprisingly simple functional forms. A commonly used Ψ_T is a product of determinant and correlation parts,

$$\Psi_T(R) = \sum_n d_n \text{Det}_n\{\varphi_\alpha\} \text{Det}_n\{\varphi_\beta\} \exp[U]. \quad (8)$$

The spin-up and spin-down Slater determinants use one-body orbitals φ_α , φ_β from various types of calculations such as Hartree–Fock (HF), multi-configuration HF or LDA. In the case of near-degeneracies more than one configuration is used to describe correctly the zero-order approximation of the wavefunction [14,15].

The correlation factor is given by

$$U = \sum_{i,j,I} u(r_{iI}, r_{jI}, r_{ij}), \quad (9)$$

where i, j and I are electron and ion labels, respectively, and r_{iI} , r_{jI} , r_{ij} denote corresponding distances.

The function $u(r_{il}, r_{jl}, r_{ij})$ is expanded in an appropriate basis set, and the expansion coefficients are iteratively optimized using configurations from VMC runs [14,16]. The optimization is usually done by minimization of the energy variance, given by

$$\sigma^2 = \frac{\langle \Psi_T | (H\Psi_T/\Psi_T - E_V)^2 | \Psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle}, \quad (10)$$

which is a more robust procedure than the minimization of the variational energy [14]. (The variational energy estimated with a finite number of statistical samples can be ill-behaved in some regions of the variational parameter space.)

A typical number of variational parameters in our calculations is ≈ 20 . Experience with the currently used functional forms of $u(r_{il}, r_{jl}, r_{ij})$ [16,17] indicates that the wavefunction improvement for more than ≈ 25 parameters is marginal.

The functional form (8) contrasts with the traditional basis set methods which expand the wavefunction in a sum of products of one-body orbitals in order to evaluate expectation values by reducing many-body integrals to few-dimensional ones. Overall, this may seem like a more viable strategy compared to the Monte Carlo estimators (1) and (7) with their inevitable error bars. However, the crucial issue is the capability of the basis set to describe the true wavefunction, and this is where the inefficiency of the basis set methods comes in.

2.4. Atomic cores

It has been repeatedly shown [13] that the treatment of atomic cores is difficult within the QMC methods. The main reason is a rapid growth of the total energy with increasing atomic number and a corresponding growth of fluctuations in the sampling process. However, for valence properties the atomic cores are essentially inert and can be considered frozen for heavier elements. In QMC the frozen cores are replaced by effective core potentials (nonlocal pseudopotentials) [6,18,19] with the corresponding change of the electron-ion part in (2). There are also alternative approaches such as the pseudo-Hamiltonian [20] method or special sampling techniques like the damped-core method [21].

Treatment of the nonlocal effective core operators requires a modification of the DMC method. This is

the consequence of the fact that the Green function with nonlocal operators may not be a positive function everywhere which is in a direct contradiction with the probabilistic interpretation invoked in Eq. (5). One option for dealing with this difficulty was proposed by Hammond et al. [19] and in a similar manner by Hurley and Christiansen [18]. In DMC, the operator which represents the nonlocal pseudopotentials, W , is replaced by

$$W \longrightarrow \frac{W\Psi_T}{\Psi_T}. \quad (11)$$

Therefore, instead of nonlocal one-body operators we have a projection onto the trial function. This, in essence, defines a new *local* effective core operator which depends on the trial function. This also means that there is no guarantee that the energy estimation will be an upper bound to the energy of the original Hamiltonian with W . However, the error introduced by this replacement vanishes quadratically in the error of Ψ_T [6]. In our calculations we were able to construct sufficiently accurate trial functions so that the effect of this localization approximation was rather small. Limited tests indicated a systematic energy shift of the order of 0.1 eV/atom for both *sp* systems and *3d* transition elements with the Ne-core pseudopotentials [15,22]. In practice, it is quite difficult to distinguish this error from the fixed-node approximation [6]. Therefore, later in the text we consider only the total DMC error which includes both these approximations.

Very recently, the treatment of nonlocal operators in DMC was advanced by ten Haaf et al. [23,24]. In their work the operator W is decomposed into W_+ and W_- , which are defined as

$$\begin{aligned} \langle R' | W_- | R \rangle &= \langle R' | W | R \rangle \Theta[\langle R' | W | R \rangle \\ &\quad \times \Psi_T(R) \Psi_T(R')], \end{aligned} \quad (12a)$$

$$\begin{aligned} \langle R' | W_+ | R \rangle &= \langle R' | W | R \rangle \Theta[-\langle R' | W | R \rangle \\ &\quad \times \Psi_T(R) \Psi_T(R')], \end{aligned} \quad (12b)$$

where $\Theta[.]$ is the Heaviside step function. The ‘sign flipping part’ W_- is then projected onto the trial function similarly to Eq. (11) while the W_+ part is actually *sampled* in the stochastic process. Therefore, the replaced effective core potential is given by

$$W \longrightarrow \int \langle R' | W_+ | R \rangle dR'$$

$$+\Psi_T^{-1}(R) \int \langle R'|W_-|R\rangle \Psi_T(R') dR'. \quad (13)$$

The interesting aspect of such a modification is that although the energy depends on Ψ_T it is always above the exact energy of the original Hamiltonian with W . Moreover, the energy converges to the exact one as Ψ_T approaches the exact eigenstate. Unfortunately, this approach does not have the zero variance property. This means that even for Ψ_T equal to the exact solution, the local energy is not an eigenvalue and will exhibit fluctuations of the order of the pseudopotential amplitude, thus decreasing the efficiency of the sampling process. However, the idea is certainly an interesting one and deserves to be tested on real chemical systems.

3. Applications

3.1. Atoms

We will present results of two atomic calculations: the electron affinity of the Sc atom [16] and excited states, ionization potential, and electron affinity for the Fe atom [15].

The Sc^- anion is rather unusual. The additional electron does not occupy the d state, like for the rest of stable $3d$ anions, but rather occupies the $4p$ state, similar to Ca^- [25]. Moreover, the state does not obey Hund's rule, and the ground state is a singlet $^1D(3d4s^24p)$. Because the $4p$ state is very weakly bounded with a very small density in the core region, we have used the Ar-core pseudopotentials with only 4 electrons in the valence space. QMC was able to reproduce Sc^- correctly, and an estimation of the electron affinity of 0.18(2) eV agrees extremely well with the experimental value of 0.19(2) eV.

The calculations of the Fe atom were done with Ne-core pseudopotentials generated within multi-configuration HF with the scalar relativistic effects included [15]. A comparison with experiment and with the most accurate quantum chemistry calculations shows that QMC is very competitive (Table 1). The overall agreement with experiment is excellent with an average error of ≈ 0.15 eV. It is interesting that none of the methods predicted correctly the small electron affinity of this element. QMC shows essentially zero affinity which means that it corrects for \approx

Table 1

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. LSDA corresponds to Local Spin Density Approximation results [47] and CCSD(T) results are from Ref. [48].

	I. IP	$^5D \rightarrow ^3F$	$^5D \rightarrow ^5F$	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

94% of the HF erroneous estimation of −2.36 eV. At the same time, this result shows the limit of accuracy of the trial function used, which for the determinantal part included only two configurations ($4s^2 \rightarrow 4p^2$) [15], and a more accurate trial function is highly desirable in this case. However, the overall performance of QMC is excellent and shows great promise for calculations of transition element systems.

3.2. Molecular systems

Very recently we have performed calculations of silicon [26] and carbon clusters [27] which enabled us to study the impact of correlation effects on the structure and stability of isomers in a range from a few to 20 atoms. These high accuracy calculations also provided interesting comparisons between QMC, other methods and experiments (Fig. 1). For example, we have found that for larger neutral Si clusters LDA describes the energy differences very reliably. On the other hand, we have discovered that LDA was not adequate for the Si_{13}^- anion, with the prediction of an incorrect ground state symmetry [26]. In addition, the QMC binding energies were within a few percent of experiment while the LDA method overbound by about 20%.

The calculations of carbon clusters [27] demonstrated much more dramatic discrepancies, especially for C_{20} isomers. In particular, the work of Raghavachari et al. [28] pointed out large differences between HF, LDA and several Generalized Gradient Approximation (GGA) functionals. Our calculations of three isomers of C_{20} in the dimerized chain, relaxed graphite bowl and distorted dodecahedron cage

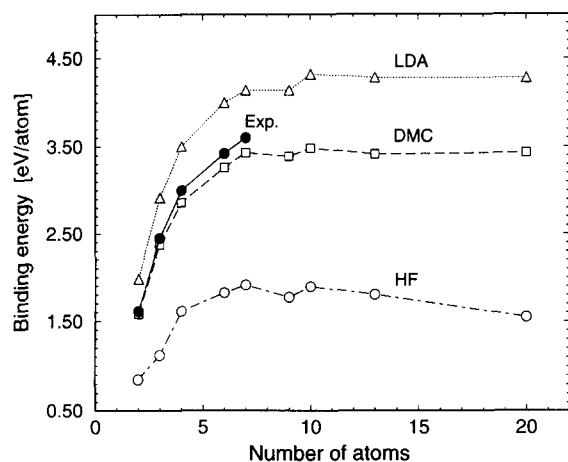


Fig. 1. Binding energy of the most stable Si clusters from HF, LDA and DMC methods compared with available experiments [26].

Table 2

The comparison of HF, LDA, DMC and experiment for the cohesive energy [eV/atom], $\Gamma \rightarrow X$ band gap and Γ point band width [eV] of diamond

Method	Cohesive energy	Band gap $\Gamma_{25'} \rightarrow X_{1c}$	Band width $\Gamma_{1v} \rightarrow \Gamma_{25'}$
HF	5.4	13.2	29.4
LDA	8.4	4.6	22.1
DMC	7.2(1)	6.0(4)	23.9(7)
Exp.	7.35	6.1	24.3

structures (Fig. 2) revealed an extremely fine interplay between the Coulomb, exchange and correlation contributions and, contrary to the LDA predictions, indicated the graphitic bowl as the lowest energy isomer [27]. Various GGAs produced varying isomer orderings between the two extreme cases represented by the LDA and HF results (Table 2). We believe that these results might have far-reaching consequences because of the importance of carbon bonding capabilities as a foundation of organic chemistry. Evidently, electron correlation plays an extremely important role in molecular carbon and crucially affects its stable and metastable geometrical conformations.

3.3. Solids

Several applications of QMC methods to solids such as silicon, diamond or germanium [9,10,29,49] demonstrated an excellent agreement of QMC cohe-

sive energies with experiments. Our calculations of excitons in large gap insulators [22,30] expanded the applicability of the QMC methods for solids beyond the ground state properties. The exciton energies, after correcting for small electron-hole interaction, enabled us to find indirect gap energies with significant improvement over the mean-field approaches. An example of such a calculation is our study of diamond [30]. The band structure shown in Fig. 3 is found by the Hartree-Fock method using the CRYSTAL package [31]. Table 3 provides a comparison of the cohesive energy, the excitation from $\Gamma_{25'} \rightarrow X_{1c}$ and also the result of an attempt to estimate the valence bandwidth at the Γ point. The bandwidth can be calculated in a similar manner as the gap. One simply calculates two excited states, $\Gamma_{1v} \rightarrow X_{1c}$ and $\Gamma_{25'} \rightarrow X_{1c}$, both of them the lowest states of different symmetries. The difference of these two excitations gives an estimation of the band width. A generalization of this idea offers interesting new possibilities for QMC studies of band structures. In addition, the combination of excited state calculations with electron addition and removal can lead to a study of excitonic effects which are of high interest, e.g., in transition metal oxides or C_{60} related materials.

4. Comparison of QMC and other methods

The presented results indicate the current strengths of QMC methods: accurate estimations of binding and cohesive energies, accurate energy differences for various structural conformations, insight into the correlation effects and their impact on structure and stability. In addition, the capability of providing total energies for a variety of systems, from atoms through molecules to solids, using the same correlated wavefunction method is unique and extremely valuable. The perspectives for studies of band structures in solids by QMC are also very encouraging.

QMC significantly improves the agreement with experiment when compared with the LDA approach, typically by a factor of 5 to 10. Moreover, the applications show that the QMC methods are competitive with the current high accuracy basis set approaches and, at the same time, can be applied to much larger systems.

Table 4 shows a comparison of the performance of the VMC and DMC methods and the HF, LDA and

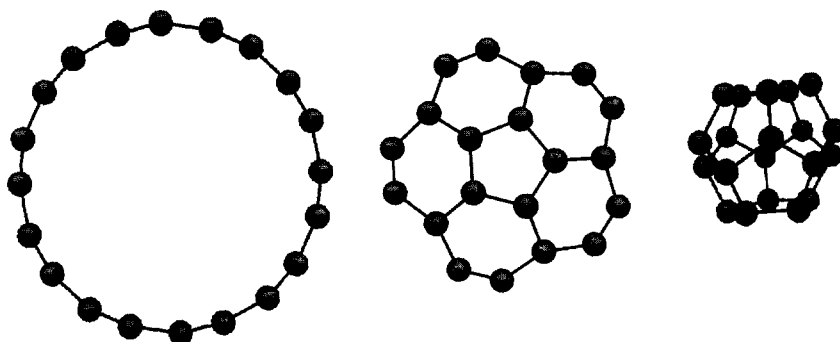


Fig. 2. Atomic structure of C_{20} isomers: dimerized ring, relaxed graphite bowl and distorted dodecahedron cage [27,28].

Table 3

The comparison of relative energies (eV) of C_{20} isomers as obtained by HF, LDA, DMC and gradient corrected functional methods [27]

	HF	LDA	DMC	B-LYP	B3-LYP	B-PW91	B3-PW91
Ring	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Bowl	1.6	−3.2	−1.1(2)	1.1	0.4	−0.5	−0.8
Cage	4.6	−4.3	1.1(2)	3.4	2.3	0.3	−0.1

Table 4

The comparison of HF, LDA, VMC, DMC and CCSD(T) methods. See text for more details.

Method	E_{corr}	E_{coh} ; E_{bind} errors	Scaling in # of corr. e^-	Total time for C_{10}
HF	0	50%	N^3	14
LDA	N/A	15–25%	N^3 (a)	1
VMC	$\approx 85\%$	2–10%	$N^3 + eN^4$ (b)	16
DMC	$\approx 95\%$	1–4%	$N^3 + eN^4$ (b)	300
CCSD(T)	$\approx 75\%$ (c)	10–15% (c)	N^7	1500 (c)

(a) recently, LDA algorithms with scaling proportional to N have been proposed [50,51].

(b) $\epsilon \approx 10^{-3}$ – 10^{-4} .

(c) with 6-311G* basis set; in the limit of infinite basis set and order of excitations the CC method is formally exact and therefore it can provide essentially exact results for small, few-atom systems. We quote results for 6-311G* basis sets and SD(T) level of excitations which was the most that we could computationally afford for the C_{10} systems.

CC approaches. This is by no means an exhaustive comparison as we have used results scattered over the literature and our own tests mostly for sp systems with a few elements such as C, N, H and Si. Therefore, the compared characteristics should be understood as *approximate typical values* (as it is not very difficult to find exceptions in any direction). Compared quantities are listed as follows:

- (i) Percentage of valence correlation energy ($E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}}$) recovered, estimated by comparisons with high accuracy calculations for small systems and by combining HF, correlated atomic

and experimental data for larger systems.

- (ii) Errors in binding or cohesive energies.
- (iii) Scaling of computational demands for total energies as a function of the number of electrons.
- (iv) Actual computational time for the C_{10} [27] cluster. We used the GAMESS code for the HF calculations and GAUSSIAN94 for CCSD(T); the target QMC error bar was 0.01 eV/atom and the absolute unit of time was 90 seconds of a Cray C90 processor.

The last quantity is quite an ambiguous one, as it depends on implementation, type of computer, etc., and

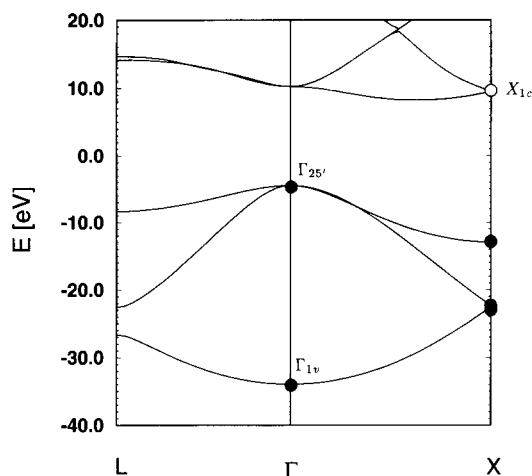


Fig. 3. Hartree-Fock band structure of diamond. The filled circles indicate states which are occupied in the 8-atom simulation supercell.

can vary easily by a factor of 3 or more. Therefore, for the computer time only the orders of magnitude are meaningful.

There are several interesting facts to notice in Table 4. For example, the VMC computational demands are very close to those of the HF method. One of the most interesting results is that relatively simple trial functions given by (7) and (8) with about 20 variational parameters consistently recover about 85% of the correlation energy for a variety of systems in the range from a few to more than 200 valence electrons. This is perhaps the strongest demonstration of the efficiency and appropriateness of the treatment of many-body effects in QMC. The remaining error of about 5% of the correlation energy for the DMC method is a consequence of the two approximations involved: the fixed-node error and the trial function projection of the effective core potentials (localization error). It is difficult to estimate the individual contributions of these two approximations [6,15], although we conjecture that the largest part is the fixed-node error. Finally, Table 4 shows an onset of the unfavorable scaling of the CCSD(T) method even for a rather small basis set.

Besides the scaling, the QMC methods have further advantages for implementation on parallel architectures. The QMC method, as a typical stochastic approach based on the accumulation of information from independent random samples, has an inherent parallelism essentially built-in. To explore this advantage

one has to parallelize along the sampling points domain, which implies that a simulation should fit into the memory of one processor. This seems not to be a restriction for the near future: we estimate that a 500 electron simulation will be feasible in such a mode with 64–128 Mb of memory per processor. The occasional communication necessary for the DMC method to stabilize the sampling points population is quite negligible. Moreover, there is a flexibility between memory, computer time and size of the sampling ensemble which can be used to optimize the calculation for a given architecture. The scalability advantage is already being explored and several groups have implemented QMC codes in parallel.

The length of the codes is another argument in favor of QMC, although to a lesser extent than it is sometimes claimed. It is true that a version of QMC for a small system with a simple trial function can be quite short (say, a few hundred lines). However, an efficient code which can deal with more complicated systems, multi-configuration wavefunctions and pseudopotentials has to be substantially longer, although still probably not of the size of an efficient quantum chemistry package.

For the convenience of the reader, we note that reviews with many thorough discussions for a range of QMC topics have been published very recently [32–34,13].

5. Tasks and challenges for the future

In this part we will mention a few research directions which we consider to be challenging, important and worth pursuing in the future.

Fermion sign problem

One of the fundamental questions for QMC is whether there exists an ‘exact’ stochastic algorithm for fermions which, for a prescribed error, scales like a low-order polynomial in the number of particles. (For boson ground states we know that this is the case [5]). The difficulty with fermions manifests in the fermion sign problem, which is in practice overcome by the fixed-node approximation [35,11] or, for small systems, by algorithms with exponential scaling [36]. There are various ways to *formally* deal with this difficulty, and claims that the fermion prob-

lem has been solved have appeared many times in the literature [37]. However, as far as we know, there is no proof that there is such an algorithm for a general many-fermion system. What has been done was the development of algorithms capable of obtaining high or very high accuracy results for small systems [38]. This was achieved by filling the electron configuration space by walkers and using symmetries to increase the efficiency of the so-called cancellation algorithms [39,13] or by the release node method [36]. Stimulating developments were suggested by Zhang and Kalos [40], with new algorithm ingredients such as coupling and biasing of the walkers in order to increase the efficiency of cancellation. The potential of these ideas for large-scale calculations remains to be investigated.

Another way of approaching this problem is through parametrizations of fermion nodes, in general, $(3N - 1)$ -dimensional hypersurfaces. Although not too much is known about these complex objects [41], and it is difficult to imagine that one will be able to parametrize the nodes in a completely arbitrary fashion, systematic improvement of the fixed-node wavefunctions would be of practical value for many applications. Currently, we understand that near-degeneracies affect the nodes significantly, which is obvious because of large weights of such configurations in the CI wavefunction expansions [14]. However, nonnegligible fixed-node errors can be detected also in cases with no significant near-degeneracy effects. The effort of Filippi and Umrigar [42] to optimize both orbitals and weights of configurations together with correlation factors for the first-row dimers provides several examples of decreasing the fixed-node error and points out the prospects of such an approach.

Clearly the fermion sign problem remains one of the most important unsolved challenges of the QMC method.

Accuracy of 0.01 eV

For some electronic structure phenomena an accuracy of ≈ 0.01 eV would be desirable. Such a goal demands a significant increase in accuracy of each component of the whole approach. In particular, one has to consider:

- (i) a more accurate treatment of atomic cores, i.e., using high accuracy pseudopotentials and/or including more electrons into the valence space and therefore decreasing the core size; another possibility is to include core-polarization and core-relaxation corrections [43];
- (ii) an algorithmic circumventing of the fermion sign problem or ability to construct more accurate trial wavefunctions with small fixed-node errors;
- (iii) an overall increase in efficiency (faster algorithms, more efficient trial functions, better sampling).

Geometries

One of the important developments which has not been implemented yet into the QMC methodology is the calculation of forces for geometry optimizations, vibrational analysis, etc. Clearly, new techniques have to be designed to overcome the handicap of error bars which complicates the evaluation of forces and Hessians. One can imagine using correlated sampling for numerical estimations of the derivatives or the direct Hellman–Feynman formulation. However, a significant amount of testing and investigation has to be carried out in either of these possibilities. A discussion on this subject can be found in the book of Hammond, Lester and Reynolds [13].

Standardization and a future impact

There are several issues which have to be addressed before a more routine use of QMC methods will take place.

First, although calculations done so far show a big span of applications, more systematic accuracy studies are desirable. It is evident that the method has to demonstrate its performance for a wide range of molecules and extended systems, and areas of efficient applicability should be understood and, ideally, quantified.

The second issue has to do with the fact that so far standards of the QMC methodology are defined rather vaguely. This, together with the statistical character of results, makes it difficult to repeat the calculations, say, by an independent code. It is evident that standards accepted, e.g., in quantum chemistry, such as basis sets, methods and ultimately extensive research tools

represented by packages such as GAMESS and others, were of high benefit for the development of that field.

Perhaps the most useful standards could be listed as follows:

- (i) methods, such as VMC, fixed-node DMC, including the Green's functions, etc.;
- (ii) functional forms and parameters of correlation factors, optimization methods;
- (iii) representation of cores such as pseudopotentials, pseudo-Hamiltonian, and their treatment in various methods, basis sets for the pseudopotentials;
- (iv) reproducible test examples.

We believe that a proper specification of at least some of these items might save some unnecessary confusion and increase productivity in the whole field.

6. Conclusions

With the advance of technology at all levels, there is a growing need for high accuracy in the description and predictions of electronic structure for materials and substances with technological potential or ecological implications. For example, developments of nanostructure materials, C_{60} related systems, clusters for catalysis or molecular drug design clearly demonstrates that technology depends on smaller and smaller energy differences, often reaching the level of a few chemical bonds and chemical accuracy. The fact that, e.g., drug and biochemistry companies actually produce a huge number of substances and then analyze their properties one-by-one indicates that the power of computational methods is rather limited. Perhaps there is less of a need for simplified approximate pictures or models and more of a need for a reliable approach (or approaches) which can deal with extremely complex systems of thousands of degrees of freedom, with an accuracy which enables predictions of equilibrium conformations, excitations, reaction barriers, etc., with an accuracy of 1 kcal/mol or even less. Perhaps we need less of the traditional reductionism and more of a new type of reductionism based on well-defined functional units (methods, algorithms, packages) which can be used as a part of other, possibly more global and complex, research efforts. We believe that the QMC approach can be one of the examples which will fit such a vision.

We hope that this article has provided some in-

sight into the recent progress of QMC methods. There is a list of remarkable achievements for the last five years: extremely high accuracy calculations of small molecules [38], treatment of hydrogen solids with inclusion of proton zero point motion [44], predictive calculations of covalent clusters with up to almost 100 valence electrons [26,27], and unprecedented correlated calculations of covalent solids including the first band gap estimations [9,22]. Further generalizations of this approach are under way: the treatment of magnetic fields with the fixed-phase method [45] and the development of the fermion Path Integral Monte Carlo method [46] which provides tools for finite temperature studies.

On the basis of these achievements we believe that QMC is becoming a new alternative and a powerful research tool for ab initio electronic structure calculations.

Acknowledgements

I am very grateful to Jeffrey C. Grossman for his contribution to the success of several projects mentioned here. I am also thankful to David Ceperley and Richard M. Martin for discussions and support. A number of the mentioned projects have been carried out at NCSA computer facilities and were supported by the NSF, DOE, ARPA and State of Illinois funds.

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