Quantum Monte Carlo studies of electronic systems

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Abstract

We review our recent work on developing and applying quantum Monte Carlo (QMC) methods to electronic systems. The "special k-points" method is introduced into QMC calculations as a method for reducing "independent particle" finite size effects. We also explain our new formulation of the Coulomb interaction which virtually eliminates so-called Coulomb finite size effects. The importance of these advances for future applications of QMC techniques to electronic systems is stressed.

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I. INTRODUCTION

Quantum Monte Carlo (QMC) methods are an attractive choice for performing highly accurate calculations on correlated systems. There are many types of QMC method, but here we will discuss only the variational quantum Monte Carlo (VMC) method [1] and the diffusion quantum Monte Carlo (DMC) method [2], applied to ground state properties at zero temperature. We use these methods mainly to study solids with (as far as possible) a realistic description of the constituent atoms.

In the VMC method the energy is calculated as the expectation value of the Hamiltonian with an approximate wavefunction, with the multi-dimensional integrals being evaluated via a Monte Carlo method. In the DMC method a distribution is generated via propagation of the imaginary-time Schrödinger equation, from which very accurate energies can be calculated. This method makes use of importance sampling, in which an approximate guiding wavefunction biases the sampling towards regions where the wavefunction is large, which reduces the variance. To make the calculations tractable the so-called fixed-node approximation [3] is normally used, in which the nodal surface of the wavefunction is constrained to be equal to that of the approximate guiding wavefunction.

Applications of these types of QMC methods to solids have used a finite simulation cell with periodic boundary conditions to reduce the number of particles to a manageable size of up to a few hundred. The computational effort is very large and applications to solids are still quite limited. The main thrust of our work has been to improve QMC techniques so that they can be applied reliably and with a reasonable computational effort in studies of real materials. Here we will discuss some of our technical developments, especially in the area of reducing the finite size effects due to the use of a small simulation cell. We will concentrate of the physics underlying these developments and illustrate their efficacy via applications to real materials.

II. ACCURATE MANY-BODY WAVEFUNCTIONS FOR SOLIDS

The quality of the approximate wavefunction determines the accuracy of a VMC calculation and, to a lesser extent, it also affects the accuracy of the DMC energy via the fixed-node approximation. In both VMC and DMC calculations the quality of the wavefunction determines the variance of the estimate of the energy. In addition, expectation values of operators which do not commute with the Hamiltonian are normally evaluated using the method of mixed estimation [2], whose accuracy depends on both the VMC and DMC expectation values. Therefore the development of accurate many-body wavefunctions is crucial for the successful application of QMC methods.

The approximate wavefunctions used for QMC calculations on solids are usually chosen to be of the Slater-Jastrow type:

$$\Psi = D^{\uparrow} D^{\downarrow} \exp\left[-\sum_{i>j} u(\mathbf{r}_i, \mathbf{r}_j) + \sum_i \chi(\mathbf{r}_i) \right] , \tag{1}$$

where $D^{\uparrow}$ and $D^{\downarrow}$ are Slater determinants of, respectively, spin-up and spin-down single-particle orbitals. The function $u(\mathbf{r}_i, \mathbf{r}_j)$ in the Jastrow factor correlates the motion of pairs of electrons, and $\chi(\mathbf{r}_i)$ is a one-body function.

Local density approximation (LDA) or Hartree-Fock (HF) orbitals have often been used to construct the determinants in Eq.(1). There is quite a lot of evidence that the charge density from LDA and HF calculations is often remarkably good, although the errors in the total energies may be large. The u function has normally been restricted to forms depending only on the distance between electrons. In a real solid the electron correlations depend on the positions of all the electrons and all the nuclei. Of course it would be impossible to include all of these dependencies in a practical correlation factor, but it is of great interest to know how well one can do with simple forms. One would also like to know whether terms correlating the motion of three electrons or two electrons and the position of a nearby nucleus are important. We have used polynomial expressions for u, which act only between an electron and its nearest periodic image [4]. We have also investigated the effect of adding a u function which correlates the motion of two electrons and the position of a nearby nucleus [4]. The effect of including u in the wavefunction is to keep the electrons further apart, which smoothes out the charge density, and the single-body χ function allows the electronic charge density to be altered in the presence of u [5]. We have used a Fourier representation for the χ function.

Having proposed a functional form for the wavefunction we must obtain the optimal values of the parameters. One possible criterion is to minimize the energy, which gives the best (lowest) value for the energy of the system. However, this method often gives poor values for other expectation values and it is widely accepted that a better strategy is to minimize the variance of the energy [6].

We have performed wavefunction optimizations for silicon and germanium (pseudo) atoms, for diamond structure silicon and germanium, and for the homogeneous electron gas over the density range r_s=0.1-10. These systems are probably representative of sp-bonded materials. The picture that emerges of electron correlations in these materials is as follows [4]. A u function depending only on the distance between electrons does a remarkably good job. The effective range of the correlations is quite small. This fact can be used to speed up the calculation as it means that it is sufficient to sum the u function only over the nearest periodic images of each electron. We have found that correlations involving the positions of two electrons and the nearest ion are unimportant in these systems. In our calculations the wavefunction is optimized as a whole and no attempt is made to constrain the charge density. Nevertheless, for silicon and germanium the charge density from the optimized wavefunction is close to the LDA form for both (pseudo) atom and solid. This implies that the LDA charge densities are good, even though the energy of the atom is rather poorly described in the LDA. Fahy et al. [5] had the idea of using χ to return the charge density to the LDA form, and our work shows that this idea is a good one, although we prefer this behaviour to arise naturally from the minimization technique. We have calculated the cohesive energy of diamond structure germanium to be 3.71 eV per atom within VMC and 3.85 eV per atom within DMC. These values compare very well with the experimental value of 3.85 eV per atom [7], and are much better than the LDA result of 4.59 eV per atom [8].

III. FINITE SIZE EFFECTS I - INDEPENDENT PARTICLE ERRORS

Using a finite simulation cell with periodic boundary conditions to represent an infinite system leads to finite size errors which we would like to make as small as possible. In past QMC calculations these errors have often been larger than the energies of interest and empirical finite size corrections have been applied. The finite size errors can be classified into two types: (1) independent particle errors, and (2) many-body or Coulomb finite size errors. It is normal to define the independent particle finite size error as the difference between the energy for the infinite and finite systems calculated within the LDA. The many-body or Coulomb finite size error is the remaining error which arises when explicit Coulomb interactions between the electrons are used, rather than evaluating the interaction energy as a functional of the charge density, as in the LDA. We have made significant progress in understanding and reducing both types of finite size error. In this section we discuss our work on independent particle corrections, while in the next section we deal with Coulomb finite size effects.

The standard method for correction of independent particle finite size errors involves using the results of LDA or HF calculations for very large systems. In practise this method seems to work rather well for the total energy, but it is still valuable to reduce these errors because we are interested in other quantities apart from the energy. Also, from the philosophical standpoint we feel that QMC calculations should stand on their own without using corrections derived from other techniques. Our advance in this area is based on the realization that the translational symmetry of the simulation cell Hamiltonian leads to two separate Bloch type conditions with two associated wavevectors. One can use the freedom to choose the values of these wavevectors to select a wavefunction for the finite system which gives a good representation of the infinite system.

The analysis starts with the standard simulation cell Hamiltonian, $\hat{H}$, for electronic systems which can be written in the form

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 + \sum_{\mathbf{R}_s}\sum_{i>j}^{N}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j - \mathbf{R}_s|} + \sum_{i=1}^{N}V(\mathbf{r}_i) \tag{2}$$

where $\mathbf{R}_s$ is the set of translation vectors of the simulation cell lattice, and N is the number of electrons in the simulation cell. Often we are interested in the case where the primitive translation vectors of the simulation cell are integer multiples of the primitive translation vectors of an underlying crystal lattice whose translation vectors are $\mathbf{R}_p$. In this case the lattice potential, $V(\mathbf{r})$, has the translational symmetry of $\mathbf{R}_p$.

The Hamiltonian $\hat{H}$ has two different classes of translational symmetry: (i) $\hat{H}$ is invariant under the simultaneous translation of all electron coordinates by a vector in $\mathbf{R}_p$, and (ii) $\hat{H}$ is invariant under the translation of any electron coordinate by a vector in $\mathbf{R}_s$. Symmetry (i) holds for the truly infinite system, but symmetry (ii) is an artefact of the use of a finite simulation cell. Each of these symmetries leads to a Bloch type condition and the eigenfunctions of $\hat{H}$ can be chosen to have well defined values of two separate wavevectors that we denote by $\mathbf{k}_s$ and $\mathbf{k}_p$ [9,10]. The two Bloch theorems are:

$$\Psi_{\mathbf{k}_s,\mathbf{k}_p}(\{\mathbf{r}_i\}) = U_{\mathbf{k}_s}(\{\mathbf{r}_i\})\ \exp\left(i\mathbf{k}_s\cdot\sum_{i=1}^{N}\mathbf{r}_i\right) = W_{\mathbf{k}_p}(\{\mathbf{r}_i\})\ \exp\left(i\mathbf{k}_p\frac{1}{N}\cdot\sum_{i=1}^{N}\mathbf{r}_i\right) \tag{3}$$

where $U_{\mathbf{k}_s}$ is invariant under the translation of any electron coordinate by a vector in $\mathbf{R}_s$ and $W_{\mathbf{k}_p}$ is invariant under the simultaneous translation of all electron coordinates by a vector in $\mathbf{R}_p$. The wavevector $\mathbf{k}_p$ is the familiar crystal momentum of the wavefunction, which can be reduced into the first Brillouin zone (BZ) of the primitive reciprocal lattice.

If the wavefunction consists of a single determinant multiplied by a Jastrow factor the values of $\mathbf{k}_s$ and $\mathbf{k}_p$ are determined by the wavevectors of the states included in the determinant. Only certain choices of these wavevectors will give determinants with definite values of $\mathbf{k}_s$ and $\mathbf{k}_p$, and it is straightforward to show that the requirement is that the wavevectors must lie on a regular mesh in reciprocal space whose translation vectors are the reciprocal lattice vectors of the simulation cell BZ. The offset of this mesh from the origin gives the value of $\mathbf{k}_s$ and the sum of the wavevectors of the individual states is equal to $\mathbf{k}_p$.

Where has all this analysis got us? The point is that we can choose the values of $\mathbf{k}_s$ and $\mathbf{k}_p$ to model the physical situation of interest. For excitation energies of the infinite solid the relevant quantum number is $\mathbf{k}_p$. Another important question is how, for a finite simulation cell, can we choose our wavefunction to represent most accurately the ground state of the infinite system? This question turns out to be intimately related to the method of "special $\mathbf{k}$-point" in bandstructure theory. This is a widely used technique for performing BZ integrations using only a small number of $\mathbf{k}$-points [11], which works extremely well when integrating over full bands, as in case of insulators. We will not go into the details here, but the conclusion is that certain values of $\mathbf{k}_s$ are much better than others. The implementation of the special $\mathbf{k}$-points method within a QMC calculation causes no particular difficulties. We have applied the technology of special $\mathbf{k}$-points to VMC and DMC calculations of diamond structure germanium [9,10], and have found it to be just as effective in QMC calculations as in independent particle bandstructure calculations. Use of this method results in greatly reduced independent particle finite size corrections for insulators.

Some illustrative results of the energy per atom of diamond structure germanium as a function of the size of the simulation cell are shown in Fig. 1. The simulation cell size is measured by n, where the simulation cell consists of $n{\times}n{\times}n$ primitive unit cells. The two sets of data joined by lines are LDA energies using the standard method ($\mathbf{k}_s = 0$, $\mathbf{k}_p = 0$), and the special k-point method ($\mathbf{k}_s = 0$, $\mathbf{k}_p = (0.5, 0.5, 0.5)$). The energies from the special k-point method converge very rapidly with system size. DMC energies for n=2 and 3 are also plotted, which show different system size errors from the LDA. These additional system size errors are Coulomb finite size errors. The point is made more clearly in Fig. 2, which shows the same results as in Fig. 1, but corrected for independent particle finite size effects using the appropriate LDA results. The LDA results now fall on a horizontal line, but the DMC results show a slowly decaying residual finite size effect. Fig. 2 also shows that applying the independent particle corrections works quite well for this system, because the corrected DMC results for the standard and special point schemes are in good agreement.

IV. FINITE SIZE EFFECTS II - COULOMB ERRORS

The slowly decaying finite size effect in the corrected DMC results shown in Fig. 2 illustrates the importance of Coulomb finite size effects. These errors are approximately inversely proportional to the number of electrons in the simulation cell. In the past they have been corrected for by performing calculations at several different system sizes and extrapolating to infinite size [12,10]. This empirical procedure is very costly and not particularly accurate.

Coulomb finite size effects are not peculiar to QMC calculations, they are present, for instance, in Hartree-Fock (HF) calculations, where they show themselves in the slow convergence of the exchange energy with the density of sampling of the Brillouin zone. These effects do not, however, occur in LDA calculations (or in other density-functional schemes). One might well ask why Coulomb finite size effects do not occur in LDA calculations, and whether by thinking in the language of density functional theory it is possible to reformulate the problem so that they are absent even when dealing with explicit Coulomb interactions between particles as in HF or QMC calculations. The absence of Coulomb finite size errors in LDA calculations is easy to understand, the electronic charge density converges quite rapidly with system size, and within the LDA the interaction energy is a functional of the charge density, so that it must converge just as rapidly. One might argue that because the model Coulomb interaction depends on the size of the simulation cell (see Eq. 2) we should use an exchange-correlation (XC) functional which depends on the system size. This logic is entirely correct if the object is to calculate the ground state energy for the Hamiltonian of Eq. 2, and in this case the Coulomb finite size error would return, but we are interested in the energy of the infinite system. In standard LDA calculations the functional calculated for the infinite system is used for *all* system sizes, which eliminates the Coulomb finite size effect.

We will now present our method for removing the Coulomb finite size effects from calculations based on explicit Coulomb interactions between particles [13]. The argument will be presented for the homogeneous electron gas (HEG).

Consider the Hamiltonian of Eq. 2 applied to the HEG. The effect of the uniform neutralizing background charge density is contained in the potential, V. This interaction energy is still not properly defined because the sum of $1/r$ interactions is only conditionally convergent, i.e. the result depends on the order of the summation. The standard procedure is to use the interaction given by the famous Ewald formula [14]. This potential is the periodic solution of Poisson's equation for the neutral system of point charges and uniform background, which is unique up to an additive constant. Two points should be appreciated here. First, we are not of course implying that one has to use the Ewald formula for calculating the potential, we use the term "Ewald" just to identify the potential we mean. Second, there are other solutions of Poisson's equation obeying different boundary conditions at infinity that we could use. One of our main conclusions is that we have found that the Ewald interaction is responsible for the large Coulomb finite size effects and that another choice of solution of Poisson's equation gives much smaller finite size effects. Furthermore we have developed a new interaction potential which is very easy to calculate and which gives essentially identical results to this "superior" solution of Poisson's equation. The new method is simpler to program, faster in computation and gives more accurate answers.

Within density functional theory the total energy of the HEG is written as the sum of kinetic and XC terms, as the Hartree terms sum to zero. The XC energy can be written as the interaction of the charge density with the XC hole. The XC hole contains an amount of charge equivalent to the absence of one electron from the hole. This sum rule holds for any proper wavefunction and does not depend on the inter-particle interaction. In a periodic simulation cell calculation we can think of a single cell as being the entire system, and therefore the XC hole is entirely confined to the cell. The effect of the finite size of the simulation cell is to distort the shape of the XC hole. However, the XC hole is often quite localized, and it is not necessary to have a very large simulation cell to describe its shape accurately. The point is that the slow convergence of the XC energy with system size in the standard formulation arises not from the convergence of the XC hole with system size, but from the convergence of the standard Ewald interaction to the correct $1/r$ potential [13].

Let us take the example of a cubic simulation cell. An expansion of the Ewald interaction potential yields

$$V_{Ewald} = \frac{1}{r} + \frac{2\pi r^2}{3\Omega} + O(r^4) \tag{4}$$

where Ω is the volume of the simulation cell. The leading term is the proper Coulomb interaction between the particles, but the second term, which is inversely proportional to the number of particles in the simulation cell, arises from the finite size of the simulation cell and (with the higher order terms) is the cause of the Coulomb finite size effects. To remove these effects in the HEG all we do is replace the Ewald interaction by a $1/r$ interaction which operates only between an electron and its nearest periodic images. The effect of the neutralizing background is incorporated by adding a constant to the interaction such that its average value is zero. This form ensures that the interaction of the electrons with their XC holes is described accurately.

For a non-uniform system the XC energy is still a short ranged quantity but there is also an important long ranged Hartree contribution. Simply taking the $1/r$ interaction between each electron and its nearest periodic image would not include the long ranged part of the Hartree interaction. The theory can be generalized to the non-uniform case, and we direct the reader to a forthcoming paper [15] for this.

V. CONCLUSIONS

We have presented the ideas behind various technical developments aimed at increasing the efficiency and accuracy of QMC calculations for solids. In the introduction we declared our ambition of developing these QMC techniques to the point where they could be applied routinely and with high accuracy to real materials. Have we achieved our aim? The answer must be that we have made significant progress but that more developments are necessary. Finite size effects have been an extremely serious issue in QMC calculations and here we can claim to have made a real contribution. The "special k-points" method is very valuable for insulating materials, but not useful for metals, so that the problem of independent particle errors is only partly solved. We have been able to virtually eliminate the troublesome Coulomb finite size effects from the problem. This will allow accurate calculations to be performed with considerably less effort than previously.

Bearing in mind the rate of technical improvements over the last few years we believe that QMC methods are becoming viable for tackling problems of interest in real materials.

VI. ACKNOWLEDGEMENTS

We thank Mei-Yin Chou, Stephen Fahy and Cyrus Umrigar for helpful conversations. Financial support was provided by the Engineering and Physical Sciences Research Council (EPSRC), UK, under grants GR/K21061 and GR/H93064. Our calculations are performed on the CRAY-T3D at the Edinburgh Parallel Computing Centre under EPSRC grant GR/K42318, the Cray YMP-8 at the Rutherford-Appleton Laboratories (UK), the Cray C-90 at the Pittsburgh Supercomputing Center (grant DMR930039P), and Hitachi Europe's SR2001 machine at the Maidenhead Remote Computing Service. Partial financial support was provided by the European Community under contract CHRX CT94-0462 via the Human Capital and Mobility Research Network on Quantum Monte Carlo Calculations for Solids.

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FIGURES

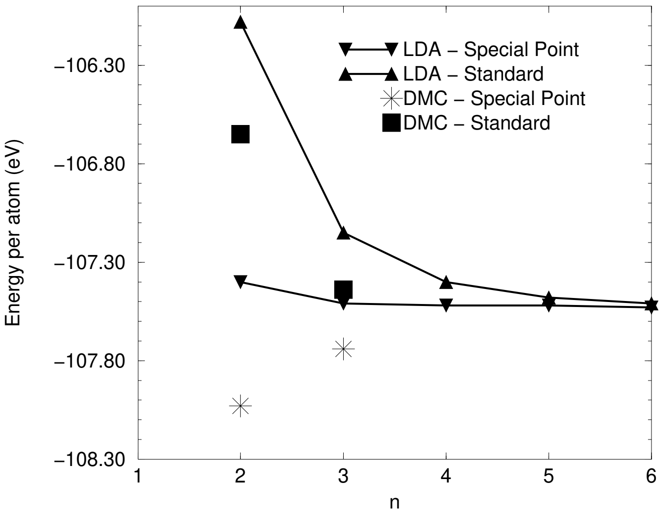

FIG. 1. The energy per atom of diamond structure germanium as a function of the size of the simulation cell, which consists of $n \times n \times n$ primitive unit cells. LDA and DMC results are shown for the standard method and the special k-points method

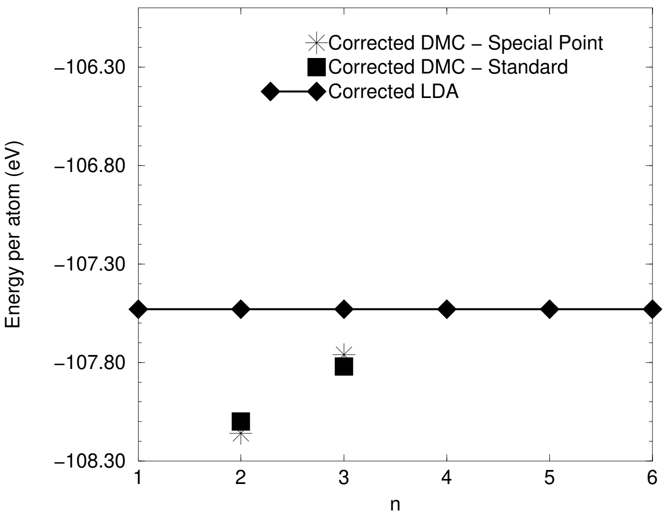

FIG. 2. The same results as in Fig. 1, but independent particle finite size effects have been applied using the appropriate LDA results.