QUANTUM MONTE CARLO CALCULATIONS ON REAL MATERIALS

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ABSTRACT

Quantum Monte Carlo methods can calculate exact or nearly exact energies and other properties of many body systems. The subject of this paper is a brief outline of some of the current developments in applying such methods to general materials and results of recent calculations. A critical issue which we discuss is the accurate treatment of core electrons, which is crucial to \textit{ab initio} calculations on materials.

1. INTRODUCTION

One of the major goals of current theoretical work is the development of computational methods for accurate \textit{ab initio} calculations of interesting properties of "real" materials, that is, molecules, crystals, surfaces, defects, artificial structures, and other types of materials of scientific and technological relevance. Since the properties are determined by the many-body system of electrons interacting with the nuclei, truly \textit{ab initio} methods must deal with this many-body problem. Quantum Monte Carlo\textsuperscript{[1]} (QMC) has an important role in reaching this goal because the statistical sampling methods used in Monte Carlo methods can simulate exactly (or nearly exactly) large many-body systems. Configuration interaction methods can find exact ground and excited states; however, they require computational time which scales as $N!$ where $N$ is the number of
particles. In contrast, Monte Carlo simulations of the ground state of a many-body system scale as $N^3$ so that they can be applied to large systems that can be scaled to the large $N$ bulk limit. In this paper we will consider QMC as a method to determine ground state properties, even though certain excited states can also be treated by QMC and projection techniques are beginning to be developed for excitations.[2] Nevertheless, this is a very important goal at the present time because the ground electronic state determines the atomic structure, phase transitions, magnetic order at $T=0$, elastic properties, defect energies, phonon frequencies, and hosts of other properties. In addition to the intrinsic interest of such ground state properties, determination of the atomic scale structure is a crucial step for *ab initio* calculations of excited electronic states.

The work described here is part of our efforts to make it possible to carry out such nearly exact calculations on general condensed matter systems. We will concentrate on variational and diffusion QMC methods, which both have crucial roles in the electronic structure problem. Since it is already well-established that such systems as hydrogen and the homogeneous electron gas can be treated by QMC, the primary new developments needed are: 1) efficient representations of the many-body trial wavefunctions for electrons in the highly inhomogeneous environments of atoms, surfaces, etc. and 2) accurate ways to treat the core electrons of elements heavier than He. These are the major subjects discussed here.

2. QUANTUM MONTE CARLO METHODS AND THE CORE PROBLEM

Among the many different types of QMC methods,[1] we will focus upon Variational Monte Carlo[3,4] (VMC) and Green's Function[5,6] (or Diffusion[7]) Monte Carlo (DMC), which are capable of treating real electron problems with the accuracy needed in condensed matter problems. VMC uses statistical sampling methods to evaluate expectation values of any operator with a correlated many-body trial wavefunction; by optimizing parameters in the wavefunction, one can find an upper bound to the exact energy and determine which types of correlations are most important among the electrons. The two great advantages of VMC are: 1) its computational and conceptual simplicity, and 2) the explicit analytic representation for the wavefunction, which makes apparent which correlations are included and which are not. The primary disadvantages are: 1) the desired correlations must be put in and 2) there is no intrinsic way to check the assumptions. Since the energy is variational one can often find good estimates of the energy; conversely, it is difficult to use energy minimization alone to find the wavefunctions since the energy is insensitive to the errors in the wavefunction.

DMC starts from a variational function and iterates the Schrodinger equa-
tion in imaginary time to project out the best possible ground state energy and correlation functions.[5,6] For Boson systems, because the ground state has no nodes, QMC methods can find the exact ground state energy and all other ground state properties. For Fermions, however, the famous "sign problem" [1] due to the antisymmetry of the particles has prevented the formulation of an exact method that is feasible for more than a few particles.[8] Nevertheless, the fixed node approximation is extremely accurate if one has a trial function with appropriate nodes. The accuracy has been established by carrying out "release node" calculations for many systems, including the homogeneous electron gas, small molecules, and solid hydrogen. [5,6,9] The primary advantages of DMC are: 1) its ability to find exact (or nearly exact) ground state energies and correlations beyond those the trial wavefunction, and 2) a greatly decreased sensitivity to the choice of the trial function. Its disadvantages are: 1) that the wavefunction is represented only implicitly in the sampling and 2) difficulties in using the fixed-node method in conjunction with non-local pseudopotentials, which as will be discussed below arise in treating atoms with cores.

Although core electrons are relatively inert, their presence has crucial effects upon the active valence electrons. The core states are problematic in sampling methods because their characteristic energy scales are large and time scales small; in DMC this causes an increase in computational time to achieve a given accuracy for the total energy which scales as $Z^{6.5}$, where $Z$ is the atomic number.[10] The reasons for this rapid increase with $Z$ is that the time scales as the cube of total number of electrons $Z^3$, with additional factors of $Z^2$ because the step size in the simulation must be decreased and $Z^{1.5}$ because of the increase in total energy. For this reason, direct calculations are not feasible even for heavy atoms, let alone molecules or solids! Our approach involves full many-body calculations on the valence electrons only, with effects of the core electrons replaced by a pseudopotential[11] (PP) or pseudohamiltonian[10,12] (PH). This breaks the problem into two parts: a) finding accurate pseudopotentials and b) simulating valence electrons moving in the non-local potentials which are more complex than ordinary local potentials. One of the primary results of recent work is that for a given PP or PH, it is indeed possible to calculate the total valence energy to a precision of order 0.05eV per atom.[13] This is sufficient for many real problems and leads to properties of Si in good agreement with experiment, including improvement of the well-known errors in the cohesive energy found in the local density approximation (LDA). Fahy, Wang, and Louie[4] were the first to carry out non-local pseudopotential calculations using VMC methods, with remarkable agreement with experiment for the cohesive energy of carbon and silicon.

The second part of our work addresses the question: how can one generate a pseudopotential or pseudohamiltonian that treats the effects of the cores with sufficient accuracy that they are worthy to be used in such accurate valence
calculations? Progress in this direction has been made in recent work,[14, 15] which has shown how to estimate the non-local term from a variational function while treating the local terms in the full fixed-node DMC. We also must face the fact that up to now pseudopotentials have been generated only in approximate one-electron methods such as LDA or Hartree Fock.[11] Any errors made in generating the potentials propagate directly into the final answers. To overcome this defect, we have recently developed methods for a more rigorous many-body "core-valence partitioning" that can be used to generate improved "quasiparticle pseudopotentials"[18,19] which are described in Section 4.

3. CALCULATIONS ON SOLIDS

In VMC one minimizes the energy with respect to a trial function, which is often chosen to have the Jastrow-Slater form:

$$\Psi(r_1, \ldots, r_N) = \exp \left[ \sum_{i=1}^{N} \chi(r_i) - \sum_{i \leq j} u(r_{ij}) \right] D(r_1, \ldots, r_N)$$  \hspace{1cm} (1)

Other more general correlated functions can be used and are essential to capture some important correlations.[15,20] The trial function is also the starting point for DMC[7] where the the operator $\exp(-tH)$ projects out the ground state from the starting trial function. Here $u(r)$ is a two body correlation function obtained from random phase approximation for a homogeneous electron gas, $\chi(r)$ is a one body term which modifies the VMC charge density,[3,4] and $D$ is a Slater determinant of single particle states. In our work LDA calculations are used in two important ways - construction of good trial orbitals and in the extrapolation to large cell size. The orbitals are taken from LDA calculations with a plane-wave basis set, including all reciprocal lattice vectors with an energy less than a cutoff.

The most extensive tests of the methods have been done on metallic hydrogen at high pressures.[16] There it was found that the Slater-Jastrow functions using LDA orbitals gives a significantly better variational energy than the previous simpler functions used by Ceperley and Alder.[9] (This was also found by Wang, et. al. [17] in their studies of H) The DMC energy was lowered slightly due to improved nodes; however, the change is much less than for VMC. We have found that for low-coordination structures not considered by Ceperley and Alder, it is important to use the LDA orbitals (and to occupy the states in the metallic system according to the LDA Fermi surface) in order to distinguish between the many structures with nearly the same energies. If the protons are held fixed then the VMC simulations for the electrons give a energies above the DMC by a nearly constant amount ($\sim 0.004 \text{ Ry}$), i.e., predict accurately the ordering of the structures. However, if the protons are treated as quantum particles, then present VMC functions are not as accurate; the energy differ-
ences are larger and the variation ($\sim 0.005$ to $0.012$ Ry) means that the VMC result cannot accurately distinguish the structures.

As a first test on other solids, calculations have been done by two groups for silicon.[4,13] We will discuss explicitly the work of Li, et. al.,[13] which was done with a cubic supercell containing 64 atoms with periodic boundary conditions. In the Slater-Jastrow wavefunction, two cutoffs for the LDA orbitals were used, 7 Ry and 15 Ry, to test the influence on the calculated energy. In VMC, the energy obtained with orbitals cutoff at 15 Ry is 0.44 eV lower than the energy with a 7 Ry cutoff, while the two DMC energies are the same within statistical errors (0.04 eV/atom.) This test suggests that the error in the nodal locations caused by the truncation of the LDA trial function is small. We use the larger cutoff in our calculations here which is more efficient because fluctuations are reduced. The difference in an LDA calculation between a 64 atom and infinite system is 0.11 eV, and our QMC results are corrected assuming that they have the same size dependence as LDA. The number of walkers in the DMC ensemble is chosen to be 200 and the initial distribution was obtained from VMC. A time step of 0.015 in atomic units was used. (This gives an acceptance ratio of 98% in the Metropolis portion of the time evolution.) A test calculation using half the time step gave identical results, showing that the time step error is less than 0.03eV/atom. A typical run with $3 \times 10^4$ steps, took 20 hours of CRAY-XMP time. To achieve the same error bars, the DMC calculation takes only 2.6 as much computer time as VMC but does not require systematic search of trial functions.

Figure 1 shows the energy as a function of lattice constant from the LDA, VMC and DMC calculations.[13] The curves are least square fits to Murnaghan equation of state. The total energy dropped 0.21(3) eV in the atom and 0.34(3) eV/atom in the solid at zero pressure (with the most accurate variational function) in going from the VMC to DMC. This difference reflects the fact that it is easier to construct a good trial function in the atom than in the solid. In VMC it is important to construct equally good trial functions at all the lattice constants, otherwise there will be a systematic bias in the results.

Also shown in Fig. 1 are the LDA total energies using the same PH. For semiconductors like silicon, LDA is known to work very well, and indeed the total energies from LDA are very close ($\sim 0.2$ eV) to those from QMC. A larger change occurs in the atom where the spin polarized LDA energy is ($\sim 0.8$ eV) higher than DMC. The difference 0.6 eV is the correction to the binding energy.

A comparison with experiment and other calculations is given in Table 1. For solid silicon, at least, LDA is working very well, and the LDA error in the cohesive energy comes mainly from using the LDA value for the energy of the atom. Our VMC energy is 0.43$\pm$0.08 eV smaller than that of Fahy, et al. If we the difference between the PH and PP as calculated by LDA, there is still a 0.2 eV difference. We performed additional VMC calculations with
Figure 1: Total energy of silicon versus lattice constant using a pseudohamiltonian (PH) from VMC (upper curve), DMC (lower), and LDA (dashed). The same corrections for finite size effects have been applied to VMC and DMC points and error bars show the estimated statistical errors.

their non-local pseudopotential, and reproduced their results. This implies that the transferability of the pseudopotentials is different between LDA and a many-body calculation such as VMC or DMC (by 0.2 eV/atom). Together with evidence discussed below, this shows that accurate construction of the pseudopotentials from a many-body theory is necessary for the full accuracy of the QMC approach to be reached.

Our DMC cohesive energy, bearing in mind the unknown transferability of the PH, should be between 4.51 (assuming no correction) and 4.73 eV (assuming the LDA gives correctly the difference between the PH and PP), in general agreement with the most quoted experimental value, 4.63(8) eV. In future work, we plan DMC calculations with a non-local “quasiparticle” pseudopotential (described below) using a new DMC method,[14,15] which treats the non-local
Table 1: Comparison of LDA, VMC, and DMC for crystalline silicon taken from Li, et. al.; using pseudopotential from Fahy, et. al.; \(^a\) from Fahy, et. al.; \(^b\) energies are in eV.

<table>
<thead>
<tr>
<th></th>
<th>a (Å)</th>
<th>B (Mb)</th>
<th>dB/dP</th>
<th>E_{at.}</th>
<th>E_{sol.}</th>
<th>E_{coh}</th>
</tr>
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<tbody>
<tr>
<td>LDA PP(^a)</td>
<td>5.373</td>
<td>0.946</td>
<td>4.00</td>
<td>-102.71</td>
<td>-108.01</td>
<td>5.30</td>
</tr>
<tr>
<td>LDA PH</td>
<td>5.455</td>
<td>0.916</td>
<td>3.93</td>
<td>-102.71</td>
<td>-107.79</td>
<td>5.08</td>
</tr>
<tr>
<td>VMC-PP(^b)</td>
<td>5.40(4)</td>
<td>1.08(10)</td>
<td>—</td>
<td>-103.42(3)</td>
<td>-108.23(6)</td>
<td>4.81(7)</td>
</tr>
<tr>
<td>VMC-PH</td>
<td>5.42(2)</td>
<td>1.08(5)</td>
<td>3.5(6)</td>
<td>-103.35(3)</td>
<td>-107.73(2)</td>
<td>4.38(4)</td>
</tr>
<tr>
<td>DMC-PH</td>
<td>5.45(2)</td>
<td>1.03(7)</td>
<td>3.8(8)</td>
<td>-103.56(2)</td>
<td>-108.07(2)</td>
<td>4.51(3)</td>
</tr>
<tr>
<td>Exp.</td>
<td>5.430</td>
<td>0.992</td>
<td>3.2-4.7</td>
<td>—</td>
<td>—</td>
<td>4.63(8)</td>
</tr>
</tbody>
</table>

parts in a variational manner.

4. QUASIPARTICLE PSEUDOPOTENTIALS

The above discussion shows that the accuracy of QMC calculations applied to real solids is now limited by the quality of the pseudopotentials used to represent the effects of the cores. However, essentially all previous pseudopotentials have been derived using a one-electron method such as Hartree-Fock or LDA.\(^{[11]}\) In one-electron methods, core and valence states are separate eigenfunctions and a pseudopotential can readily be derived which reproduces the valence function outside the core. In a many-body theory it is not clear \textit{a priori} how to make such a separation since all electrons are identical. We have devised a way to do this "core/valence partitioning" taking into account the exchange and correlation between the core and valence electrons.\(^{[18]}\)

The essence of this core/valence partitioning method is to treat the valence electrons as "quasiparticles" with self-energies which reflect the effects of the cores, i.e., exchange, dynamical correlation, and relaxation. These effects are calculating in the atom (or ion) using the Greens function method\(^{[21]}\) which is a variant of Hedin’s GW approximation, based upon the generalized RPA, which we term generalized GW (GGW). Diagrammatic summation is successful for describing the effects of cores because the large gap for core excitations makes the sums converge rapidly.\(^{[18]}\) The result is that the Green’s function for electron addition and removal in the range of valence energies can be described by valence electrons moving in the presence of frozen core orbitals plus a self-energy described by a "core polarization potential" \(V_{cp}\) which takes into account core relaxation and dynamic correlation. The form of \(V_{cp}\) was chosen following the work of Muller, et. al.\(^{[22]}\) In addition, core polarization modifies the electron-electron interaction in a simple way near the ion cores. Finally, usual methods\(^{[11,19]}\) can be used to transform this to a non-local pseudopo-
Table 2: Removal energies (in eV) for one electron bound to a core from experiment, the full atom generalized GW (GGW), the quasiparticle pseudopotential (GGW/PP) derived from the GGW, Koopman's eigenvalue (HF), self-consistent HF, and pseudopotential local spin density (LDA PP). (from Shirley, et. al.)

<table>
<thead>
<tr>
<th></th>
<th>Be 2s</th>
<th>Be 2p</th>
<th>Na 3s</th>
<th>Na 3p</th>
<th>Sc 4s</th>
<th>Sc 4p</th>
<th>Sc 3d</th>
<th>Sc 4f</th>
</tr>
</thead>
<tbody>
<tr>
<td>GGW</td>
<td>18.21</td>
<td>14.25</td>
<td>5.11</td>
<td>3.03</td>
<td>21.56</td>
<td>17.00</td>
<td>24.53</td>
<td>7.77</td>
</tr>
<tr>
<td>GGW/PP</td>
<td>18.21</td>
<td>14.25</td>
<td>5.12</td>
<td>3.03</td>
<td>21.58</td>
<td>17.01</td>
<td>24.54</td>
<td>7.77</td>
</tr>
<tr>
<td>HF</td>
<td>18.13</td>
<td>14.14</td>
<td>4.96</td>
<td>2.98</td>
<td>20.90</td>
<td>16.57</td>
<td>23.09</td>
<td>7.69</td>
</tr>
<tr>
<td>HF-SCF</td>
<td>18.13</td>
<td>14.14</td>
<td>4.96</td>
<td>2.98</td>
<td>20.97</td>
<td>16.60</td>
<td>23.76</td>
<td>7.69</td>
</tr>
<tr>
<td>LDF PP</td>
<td>18.30</td>
<td>14.61</td>
<td>5.30</td>
<td>3.20</td>
<td>21.34</td>
<td>16.91</td>
<td>25.12</td>
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The potential valence-only problem.

The first test of the "quasiparticle" pseudopotential is for one electron outside a core. In that case the valence problem is a simple one-electron problem and the eigenvalue of the "quasiparticle" pseudopotential should agree with the experimental binding energy of the electron in the exact many-body atom. Representative examples of results on atoms showing accuracy of our potential are given in Table 2. The row labelled GGW shows the results of full atom GGW calculation; the next row (GGW/PP) shows the small errors introduced in the pseudopotential transformation. Both agree very well with experiment compared to the single body methods listed below in the table. We see the the new quasiparticle pseudopotential has substantial improvements over LDA or HF derived potentials. The errors shown in Table 2 for the one electron potentials will propagate in any many-body valence calculation which uses them.

The goal, however, is to apply these potentials to many-valence-electron systems such as molecules and solids. As a critical test,[18] we have carried out a Monte Carlo simulation of the binding curve for the Na dimer - which gives the exact energy for this two-valence-electron system. Parallel calculations have been done with HF, LDA, and GGW "quasiparticle" pseudopotentials. Figure 2 shows the nearly exact agreement of the QMC calculation using the GGW potential with the experimental binding curve for the dimer. In contrast, the curves with the HF generated pseudopotential are too weakly bound (0.02eV) with equilibrium distance about 5% too large. Results with an LDA generated potential[18] are overbound by a larger amount, 0.1 eV.[19]
Figure 2: DMC energies with error bars for the Na₂ dimer using the GGW quasiparticle pseudopotential, compared to experiment. Comparison with HF and LDA pseudopotentials is described in the text.

5. SURFACES

What has been done on materials, beyond perfect crystals and simple molecules? As a first step Li, et. al.[23] have looked at the simplest surface problem, the jellium surface. The jellium surface at the density of aluminum (r_s = 2.1) was chosen because there are good arguments that this is an excellent approximation to real Al and because the results can be compared directly with other theoretical calculations. [24] For this density, the calculated surface energy is rather close to the LDA result (closer than to the previous many-body hypernetted chain calculations[24]) and is in remarkable agreement with recent gradient-corrected LDA calculations.[25] This is example of the advantages of the DMC method. In this case, the variational calculations were rather poor because it is difficult to find good analytic representations for electron correlations near the surface. Although the VMC charge density is poor, this is corrected by DMC. Examples of the electron correlation and exchange holes and their distortion near the surface have been found;[23] these could serve as
the basis for constructing new improved correlated wavefunctions for electrons at the surfaces of metals.

6. CONCLUSIONS
There are two primary conclusions of our work. The first is that given a pseudopotential or pseudohamiltonian, DMC calculations for valence electrons only can be carried out with an absolute accuracy of order 0.05 eV per atom in a real solid.[13] The precision can be better and the fundamental limitation is the fixed node approximation, for which the error has been estimated to be of this order in atomic and molecular calculations. However, there are still developments required to have effective methods to carry out fixed node calculations with non-local potentials.[14,15] The second conclusion is that promising results have been found using a new approach to "core/valence partitioning" that leads to "quasiparticle pseudopotentials."[18,19] These have been derived for atoms using many-body Green's function methods to determine the self-energy of a valence electron due to exchange and correlation with the core. Tests have shown the new potentials are transferable and predict many different states of atoms and binding of the Na dimer more accurately than potentials derived from single body methods like Hartree-Fock or LDA. Together these results are promising for accurate an initio calculations on molecules and solids.

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References


[7] Some authors distinguish between GFMC and DMC. Our DMC calculations use a short time approximation to the Green's function (see Ref. [6]), and we have tested that the time step is small enough that this is not an essential approximation.


[15] L. Mitáš, in Computer Simulations in Condensed Matter Physics IV, ed. D. P. Landau, Springer (1992); earlier references on approaches to deal with core electrons and non-local potentials in QMC are given in this paper.


