QUANTUM MONTE CARLO CALCULATIONS ON MATERIALS:
TESTS ON CRYSTALLINE SILICON AND THE SODIUM DIMER

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INTRODUCTION

Quantum Monte Carlo (QMC) is a general method to calculate the exact (or nearly exact) ground state energy and correlation functions of a many-body quantum system.[1] Green's Function Monte Carlo (GFMC) can find exact results for Boson systems; however, for Fermions the famous "sign problem" has prevented the formulation of an exact method that is feasible for more than a few particles. 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. [2,3,4]

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. The obstacles to be overcome are caused by the presence of core electrons. Although they are relatively inert, core electrons have crucial effects upon the active valence electrons. (The ideal would be to devise a theory that involves only valence electrons, yet takes into account all effects of the cores and respects the fact that all electrons of the same spin - core and valence - are in fact identical.) The core states are problematic because their characteristic energy scales are so large and time scales so small; in GFMC 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.[5] For this reason, direct calculations are not feasible for heavy atoms, let alone solids! Our approach involves full many-body calculations on the valence electrons only, with effects of the core electrons replaced by a pseudopotential[6] (PP) or pseudohamiltonian[5] (PH). One of our primary results 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.[7] 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).[8] Fahy, Wang, and Louie[9] have also done VMC pseudopotential calculations using the same types of trial functions as considered here.

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? One point is that the pseudohamiltonian approach cannot be applied in all cases[5,7,10] and the non-local potentials, which are more general, are not consistent with the fixed node approach in GFMC. Progress in this direction has been made in recent work,[11] which has shown how to estimate the non-local term from a variational function while treating the local terms in the full fixed-node GFMC. 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.[6] 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 incorporates core-valence exchange and correlations into a self-energy for the valence states.[12] The most convenient form of the results are "quasiparticle pseudopotentials"[12,13] which can be used as readily any non-local pseudopotential (with only a change requiring a simple modification of the electron-electron interaction). We have tested our pseudopotentials by essentially exact valence-only CI and QMC calculations on many atoms and on the Na_2 dimer.[12,13] Comparison with experiment shows excellent agreement in many cases and significant improvements over previous one-electron type pseudopotentials in essentially all cases.

CALCULATIONS ON SOLIDS

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

$$\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N) = \exp\left[\sum_{i=1}^{N}\chi(\mathbf{r}_i) - \sum_{i\leq j}u(r_{ij})\right]D(\mathbf{r}_1,\ldots,\mathbf{r}_N) \tag{1}$$

The trial function is also the starting point for GFMC[14] 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[2]; $\chi(\mathbf{r})$ is a one body term which modifies the VMC charge density[9] and D is a Slater determinant of single particle states. In our work to make a practical algorithm, 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 the "energy cutoff." We have used two energy cutoffs, 7 Ry and 15 Ry to test the influence on 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 GFMC 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 present results are calculated with a cubic supercell containing 64 Si atoms with periodic boundary conditions. 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 GFMC 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 3×10^4 steps, took 20 hours of CRAY-XMP time.

Fig. 1 shows the energy as a function of lattice constant from the LDA, VMC and GFMC calculations. The curves are least square fits to Murnaghan equation of state.[15] 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 GFMC. 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. To achieve the same error bars, the GFMC calculation takes only 2.6 as much computer time as VMC but does not require systematic search of trial functions.

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 GFMC (even closer to those of VMC). Although these differences are not negligible, the largest change is in the atom where the spin polarized LDA energy is about 0.8 eV higher than GFMC.
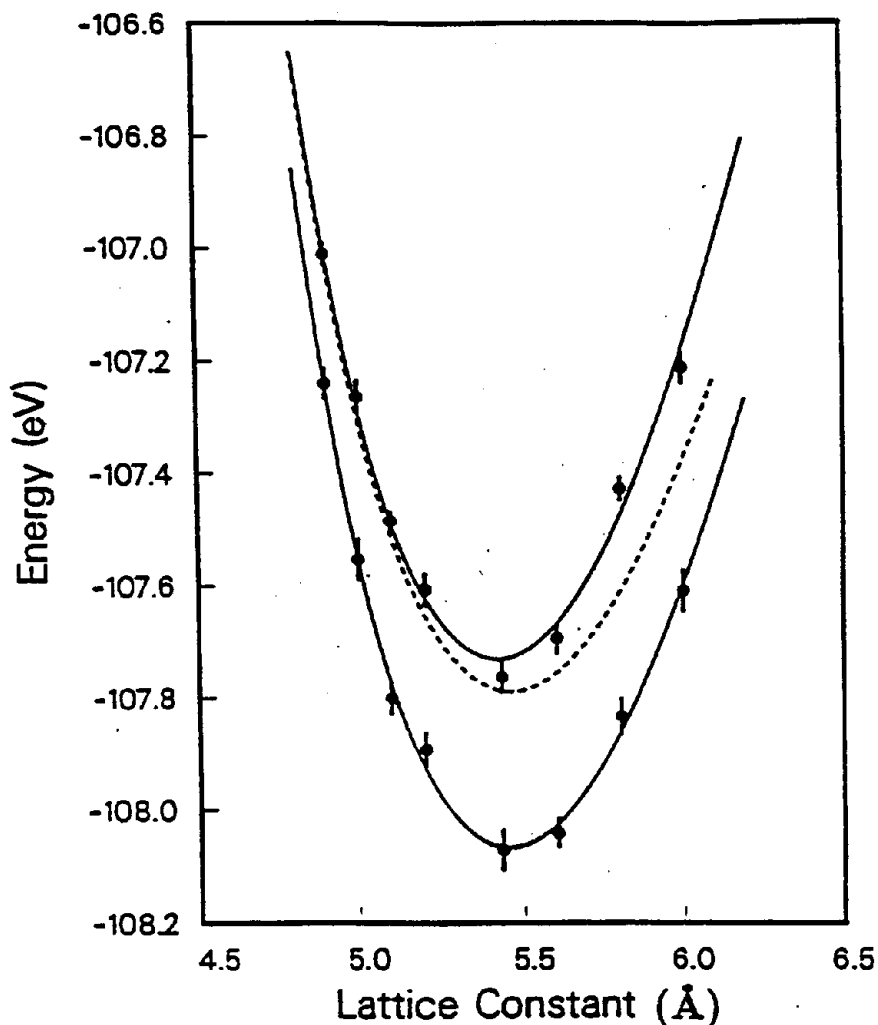

Fig. 1. Total energy of silicon versus lattice constant. The upper curve with error bars is from VMC and the lower from GFMC. Both have been corrected for the finite size of the system using LDA. The error bars show the estimated statistical errors. The solid lines are the fits to the Murnaghan equation of state. The dashed line represents the results of an LDA calculation with the same PH.

Table I. Comparison of the GFMC and VMC results with experiment and other calculations. All quantities have been corrected for finite size effects, zero point motion of the Si ions but here are no corrections applied to the difference between the pseudo- Hamiltonian and the pseudo-potential. Footnotes: [a] Our calculation using the pseudopotential from Ref. 8 with an energy cutoff of 30 Ry. [b] Fahy, *et. al.*, Ref. 9. [c] At T=0 K, Y. Okada and Y, Tokumaru, J. Appl. Phys. 56, 314(1984). [d] At T=0 K, J.J. Hall, Phys. Rev. 161, 756(1967). [e] Landolt-Börnstein: Numerical Data and Functional Relationships Science, New Series, Vol.3, 17:a, (Springer, New York, 1982). [f] JANAF Thermodynamical Tables, 3rd ed., J. Phys. Chem. Ref. Data 14, Suppl. 1, 1795(1985); and B. Farid and R. W. Godby, Phys. Rev. B43, 14248(1991).

	a_0 (eV)	B_0 (Å)	dB_0/dP	$E_{at.}$ (eV)	$E_{sol.}$ (eV)	E_{coh} (eV)
LDA PP[a]	5.373	0.946	4.00	-102.71	-108.01	5.30
LDA PH	5.455	0.916	3.93	-102.71	-107.79	5.08
VMC-PP[b]	5.40(4)	1.08(10)	—	-103.42(3)	-108.23(6)	4.81(7)
VMC-PH	5.42(2)	1.08(5)	3.5(6)	-103.35(3)	-107.73(2)	4.38(4)
GFMC-PH	5.45(2)	1.03(7)	3.8(8)	-103.56(2)	-108.07(2)	4.51(3)
Exp.	5.430[c]	0.992[d]	3.20–4.68[e]	—	—	4.63(8)[f]

The final comparison with experiment and other calculations is given in Table I. 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 ± 0.08 eV smaller than that of Fahy, et al. After correcting for 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 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 GFMC (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.

The structural properties from GFMC are in slightly better agreement with experiment than the VMC results of Fahy, et al. Our GFMC 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 (see Table caption). In future work, we plan GFMC calculations with a non-local "quasiparticle" pseudopotential (described below) using a new method,[11] which treats the non-local parts in a variational manner.

QUASIPARTICLE PSEUDOPOTENTIALS

As the work above has demonstrated, 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 work to derive theoretical pseudopotentials has been in the context of a one-electron method such as Hartree-Fock or LDA.[6] In a one-electron method it is straightforward to carry out this operation because 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 *a priori* how to make such a separation. We have devised a way to do this "core/valence partitioning" taking into account the exchange and correlation between the core and valence electrons.[12]

The essence of our 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[16] which is a variant of Hedin's GW approximation, based upon the generalized RPA. We call our way of including vertex corrections the generalized GW (GGW) which is fully conserving.[17] The basic reason that summing diagrams is successful in describing the effects of cores is that the large gap for core excitations makes the sums converge rapidly.[12] 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.[18] In addition, core polarization modifies the electron-electron interaction in a simple way near the ion cores. Finally, usual methods[6,13] can be used to transform this to a non-local pseudopotential 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 II. The row labelled GGW shows the results of our 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. This is a necessary, but not sufficient test for any pseudopotential, and we see the the new quasiparticle pseudopotential has substantial improvements. Conversely, the errors shown in table II for the one electron methods will propagate in any many-body valence calculation which uses them.

Table II. 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).

	Be 2s	Be 2p	Na 3s	Na 3p	Sc 4s	Sc 4p	Sc 3d	Sc 4f
Expt.	18.21	14.25	5.14	3.04	21.58	16.99	24.73	7.76
GGW	18.21	14.25	5.11	3.03	21.56	17.00	24.53	7.77
GGW/PP	18.21	14.25	5.12	3.03	21.58	17.01	24.54	7.77
HF	18.13	14.14	4.96	2.98	20.90	16.57	23.09	7.69
HF-SCF	18.13	14.14	4.96	2.98	20.97	16.60	23.76	7.69
LDF PP	18.30	14.61	5.30	3.20	21.34	16.91	25.12	—

Fig. 2. GFMC calculations of energy vs. distance for the two-valence electron Na dimer and the GGW quasiparticle pseudopotential. Points with error bars are the theoretical results compared to the experimental curve derived from spectroscopic data. Comparison with HF and LDA pseudopotentials is described in the text.
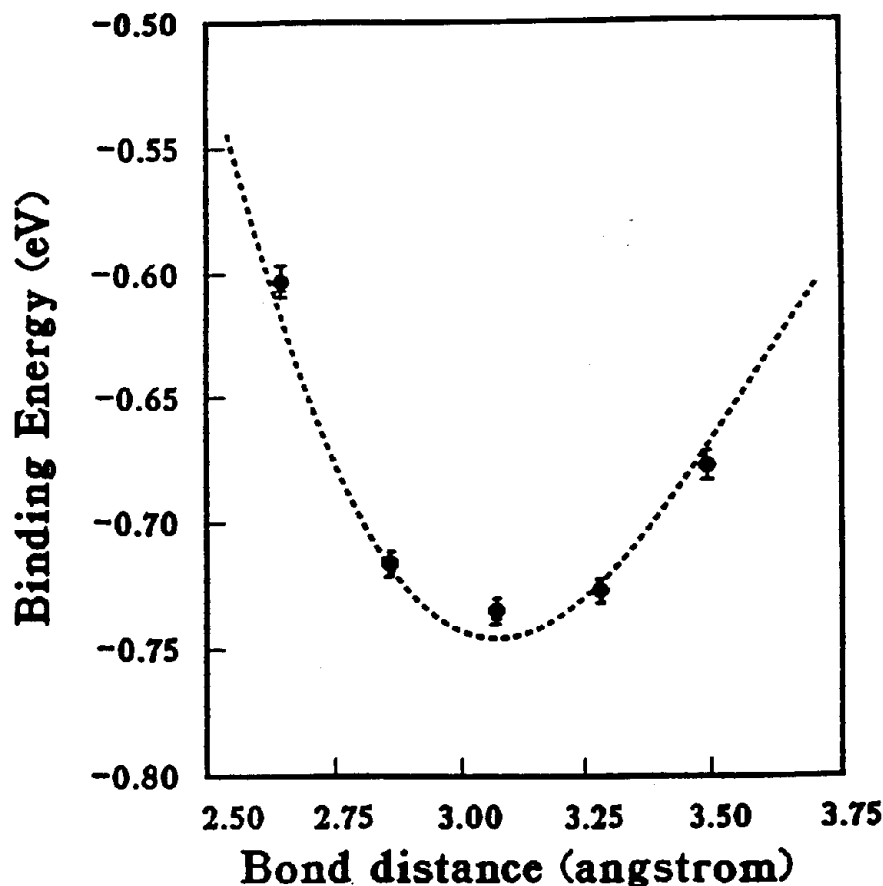
Our goal, however, is to apply these potentials to many-valence-electron systems such as molecules and solids. This involves also the changes in the e-e interactions and static core relaxations. We have carried out one nearly exact Monte Carlo simulation to test the quality of the results: the binding curve for the Na dimer. This is a two-valence-electron system which can be solved exactly by QMC. Parallel calculations have been done with different pseudopotentials[12] - ones derived from the atom in the Hartree-Fock approximation, our GGW "quasiparticle" pseudopotentials plus e-e and static core polarization terms, and LDA potentials. 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[12] are overbound by a much larger amount, 0.1 eV.[13]

CONCLUSIONS

There are two primary conclusions of our work. The first is that given the pseudopotential, the valence electron calculation can be carried out with an absolute accuracy of order 0.05 eV per atom in a real solid.[7] 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.[11] The second conclusion is that promising results have been

found using a new approach to "core/valence partitioning" that leads to "quasiparticle pseudopotentials."[13,12] 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.

ACKNOWLEDGEMENTS

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