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VARIATIONAL QUANTUM MONTE CARLO CALCULATION OF ELECTRONIC AND STRUCTURAL PROPERTIES OF CRYSTALS

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ABSTRACT

Calculation of the electronic and structural properties of solids using a variational quantum Monte Carlo nonlocal pseudopotential approach is described. Ionization potentials and electron affinities for atoms, and binding energies and structural properties for crystals are found to be in very good agreement with experiment. The approach employs a correlated many-electron wavefunction of the Jastrow-Slater form and the exact Coulomb interaction between valence electrons. One- and two-body terms in the Jastrow factor are used and found necessary for an accurate description of the electron-electron energy for the systems considered. The method has further been applied to compute various single-particle properties for solids including the single-particle orbital occupancy, electron pair correlation functions, and quasiparticle excitation energies.

1. Introduction

In calculation of materials properties, as in the case of atoms and molecules, accurate treatment of electron correlations is essential. With the exception of several recent works,[1-3] present-day ab initio methods for solid-state systems treat many-electron effects by employing basically either 1) the local density functional (LDA) formalism or 2) some type of Hartree-Fock (H-F) plus correlation corrections approach with the corrections usually determined by perturbation theory. The LDA is by far the more popular approach whereas H-F plus corrections calculations have been mostly restricted to the binding energy of insulating crystals composed of the lighter elements. The local density functional approach[4] has been applied to a wide range of materials with much success on various ground-state properties that are obtainable from relative changes in total energies. The LDA, however, has problems in giving accurate absolute cohesive energies, properties of systems with highly correlated electrons (such as the d and f electron

systems), and electron excitation energies.[5]

In this paper, we discuss a recently developed variational quantum Monte Carlo (QMC) pseudopotential approach[3] to the problem of electron correlations in solids. A trial wavefunction of the Jastrow-Slater form with one- and two-body correlation terms is employed. The total energy of the system is evaluated using the Metropolis sampling techniques[6] and the exact electron-electron interaction, thus allowing the treatment of valence electron correlations going beyond standard self-consistent field methods. A pseudopotential scheme which incorporates the effects of the core electrons in the ionic potential is also employed. The use of pseudopotentials for the electron-ion interaction removes from the problem the large fluctuations of electron energies in the core region and makes practical the present approach for systems with heavier elements.

We have applied the method to calculate the cohesive and structural properties of diamond, graphite, and Si and the ionization energy and electron affinity of the atoms. The results are shown to be in excellent agreement with experiment. In particular the cohesive energy is a significant improvement over those obtained from the standard local density functional calculations. Further, the calculations have provided results on quantities such as the single-particle orbital occupancy and electron pair correlation functions for real crystals.

2. Theoretical Method

2.1. Pseudopotential and Variational Quantum Monte Carlo Approach

The basic idea here is to obtain the ground-state wavefunction using the variational principle and from it the other properties of the crystal. The total energy of the system is evaluated using the exact Hamiltonian with a trial many-electron wavefunction. If the trial wavefunction is chosen with sufficient insight, we obtain not only an upper bound for the energy, but an accurate estimate of its value and the wavefunction itself. From the total energy as a function of the atomic coordinates, one obtains as usual the binding energy and the static structural properties of the solid. From the optimal wavefunction, a host of other quantities may also be calculated which include the charge density, the single-particle density matrix, the pair correlation function, and the quasiparticle excitation energies.

The variational quantum Monte Carlo approach was pioneered by McMillan to study liquid He^4 in 1965[7] and later extended to Fermion liquid systems by Ceperley, Chester and Kalos in the 1970's.[8] Recently, the Green's function quantum Monte Carlo approach has been applied successfully to the electron gas[9] and to light molecules.[10] However, the application of these methods to real crystals had not been realizable until very recently.[11] A number of conceptual and technical problems have to be overcome. These include the proper treatment of

the single-particle orbitals in the presence of electron correlations and the problem of the very rapid growth in the required computation time with increasing atomic number Z. This growth which scales at least as Z^5 is caused primarily by the fluctuations in the electron energy in the atomic core region.[12]

To avoid the core fluctuations problem, we adopt a pseudopotential scheme which replaces the effects of the core electrons by an ionic potential. The pseudopotential has proven very successful[13] in treating many solid-state systems within local density functional theory. The ionic pseudopotentials used here are the norm-conserving pseudopotentials generated for LDA calculations.[14] These ionic potentials in general are nonlocal of the form

$$V_{pseudo} = V_{ion}^{loc}(\vec{r}_i) + \sum_{\ell} \int_0^{\infty} dr\, V_{\ell}(r) P_{\ell,r}^{i} \tag{1}$$

acting on an electron with coordinates $\vec{r}_i$ from the ion core. Here $V_{ion}^{loc}(\vec{r})$ is the local part of the pseudopotential and $P_{\ell,r}^{i}$ is the angular momentum ℓ projection operator.

The integral operator which arises in the nonlocal pseudopotential makes the present problem different from previously considered QMC problems. However, as discussed later, this operator can be evaluated statistically within the variational QMC method using a special point scheme with a computational effort comparable to that for the kinetic energy.

2.2. The Many-Electron Wavefunction

For the trial many-electron wavefunction, we use the Jastrow-Slater form[8]:

$$\psi(\vec{r}_1,\ldots,\vec{r}_N) = \exp\left\{\sum_{i=1}^{N} \chi(\vec{r}_i) - \sum_{i<j} u(r_{ij})\right\} D(\vec{r}_1,\ldots,\vec{r}_N) \tag{2}$$

where D is a Slater determinant of single-particle orbitals. In the present calculations, the LDA Kohn-Sham single-particle orbitals are used. The exponential correlation (Jastrow) factor contains both a one-body and a two-body term. The two-body term $u(r_{ij})$, lowers the energy by reducing the probability of two electrons coming close together. The one-body term $\chi(\vec{r}_i)$ could be formally incorporated into the Slater determinant. However, it is convenient in the calculation to keep χ in the Jastrow factor using it to vary the electron density to minimize the energy.

The two-body function $u(r_{ij})$ in the Jastrow factor is chosen for the solid to be of the form[15]

$$u(r) = A(1 - e^{(-r/F)})/r \tag{3}$$

where A and F are spin-dependent variational parameters. The variational QMC approach has been successfully applied to the uniform electron gas[15] using Eq. (2) for Ψ with $X = 0$ and a two-body term u of the above form. The obtained results are shown to be highly accurate as compared to those of the more exact Green's function QMC calculations[9]. The form of u in Eq. (3) has the expected behavior: u is large and positive for $r = 0$ and decreases with increasing r. The general asymptotic form of u is, in fact, constrained by physical considerations of the Coulomb interaction. As discussed in previous work on the uniform electron gas, at large r, u is dominated by the zero-point motions of the plasmons leading to a 1/r dependence with coefficient given by $e^2/\hbar\omega_p$. There is also a "cusp" condition on u(r), owing to the singularity of the Coulomb interaction as $r \to 0$. These two conditions give some guidance in the search for the values of A and F. In the calculations, we find that the optimal values of A and F are, indeed, very closed to the values given by the physical considerations for the crystals examined. For atoms, in addition to the form of u(r) for the solid [Eq. (3)], we also have used a form of

$$u(r) = -\frac{ar}{(1 + br)} \tag{4}$$

and obtained identical energies within statistical noises.

The one-particle term $X(\vec{r})$ in the Jastrow factor serves to allow a variational relaxation of the electron density in the presence of the two-body $u(r_{ij})$ term which tends to make the electron density overly diffuse. We find that, although the one-body term is irrelevant in homogeneous systems such as liquids or the uniform electron gas, it is quite important for atoms and solids. There are several possible implementations of X [16]. For simplicity of calculation, we have either set

$$X(\vec{r}) = \frac{\alpha}{2} \ln \frac{\rho_{X,u=0}(\vec{r})}{\rho_{X=0}(\vec{r})} \tag{5}$$

where $\rho(\vec{r})$ is the electron density and α is a variational parameter, or in the case where the LDA electron density might be significantly different from the X=0 QMC density, $X(\vec{r})$ is iteratively obtained by setting

$$X(\vec{r}) = \sum_{i=1} X_i(\vec{r}) \tag{6}$$

where X_1 is given by Eq. (5) and $X_{i+1}(\vec{r}) = \alpha/2 \ln[\rho_{X,u=0}(\vec{r})/\rho_{X_i}(\vec{r})]$. For the systems considered, we find that the optimal value for α is very close to 1. This is not unexpected since the LDA charge density is generally in excellent agreement with experiment[13].

2.3. The Hamiltonian and Total Energy

For a given many-electron wavefunction $\psi(R)$, we obtain the expec-

tation value of an operator F by evaluating the multi-dimensional integral:

$$\langle\psi|F|\psi\rangle = \int F(R)|\psi(R)|^2 \, dR \tag{7}$$

where $R = \{\vec{r}_1, \vec{r}_2, \ldots \vec{r}_N\}$ is a point in configuration space specified by the coordinates of all the electrons. For the total energy, the function F(R) is then taken to be $[H\psi](R)/\psi(R)$ where H is the Hamiltonian operator. Since typically several hundred electrons in a box (corresponding to tens of atoms) with periodic boundary conditions are required to simulate accurately the properties of solids, the only practical way of evaluating many-body integrals of the form in Eq. (7) is by the Metropolis Monte Carlo algorithm[6] for importance sampling with the importance function given by $|\psi(R)|^2$.

The many-electron Hamiltonian for the crystal

$$H = \sum_{i=1}^{N} \left\{ \frac{\hbar^2}{2m} \nabla_i^2 + V_{ext}(\vec{r}_i) + \frac{1}{2} \sum_{j \neq i} \frac{e^2}{r_{ij}} \right\} \tag{8}$$

is consisted of the usual three terms: the kinetic energy of the valence electrons, the external potential due to the ion cores, and the Coulomb repulsion between the valence electrons. In the Metropolis scheme, $E(R) = [H\psi](R)/\psi(R)$ is evaluated along a random walk in configuration space so as to visit points R with probability density equal to $|\psi(R)|^2$. The average of E(R) over this walk is then an unbiased estimator of the total energy:

$$E = \langle\psi|H|\psi\rangle \simeq \frac{1}{M} \sum_{i=1}^{M} E(R_i) \quad . \tag{9}$$

As in the electron gas case, the evaluation of the electron-electron energy at each step of the walk may be carried out straightforwardly using Ewald summation techniques provided some care is given to the periodic boundary conditions imposed on the finite simulation region. Similarly, although the single-particle orbitals in the Slater determinant are no longer plane waves, the form of ψ in Eq. (2) allows the kinetic energy to be calculated using techniques developed for the electron gas[16].

The evaluation of the external potential energy is more involved because of the nonlocality of the pseudopotential. The local part is straightforward since it is diagonal in the coordinate representation of the electrons given by

$$V_{loc}(\vec{r}_i) = \sum_{\vec{R}_{ion}} V_{ion}^{loc}(\vec{r}_i - \vec{R}_{ion}) \tag{10}$$

where $\vec{R}_{ion}$ are the positions of the ions in the crystal. The value of the local potential at each configuration on the random walk is also evaluated using Ewald summation techniques. The nonlocal part (second term in Eq. (1)) is a more complicated form, and the evaluation of the

nonlocal energy involves the many-electron wavefunction on a sphere about each atom. For an ion core at the origin, the contribution from the angular momentum potential $V_\ell(\vec{r})$ to the energy of the ith electron for a given configuration $R = \{\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N\}$ is

$$E_\ell^i(\vec{r}_1, \ldots, \vec{r}_i = \vec{r}, \ldots, \vec{r}_N) =$$

$$V_\ell(r) Y_{\ell o}(0,0) \int_{r'=r} Y_{\ell o}^*(\Omega_{\vec{r}'}) \frac{\psi(\vec{r}_1, \ldots, \vec{r}_i = \vec{r}', \ldots, \vec{r}_N)}{\psi(\vec{r}_1, \ldots, \vec{r}_i = \vec{r}, \ldots, \vec{r}_N)} \, d\Omega_{\vec{r}'} \qquad (11)$$

where $\Omega_{\vec{r}'}$ is the angular coordinate of $\vec{r}'$ with $\vec{r}$ pointed along the polar axis. In principle, the expression for the nonlocal energy due to one atom in Eq. (11) should be summed over all the atoms in the crystal to give the total nonlocal energy for the ith electron. In practice, one needs only to sum the potentials of at most two neighboring atoms because the $V_\ell(r)$'s are, in general, very short range ($\simeq$ 2 a.u.). However, even with this simplification, it is impractical to evaluate the nonlocal terms using standard fixed-grid methods. We find that the integral in Eq. (11) can be evaluated accurately in a statistical fashion using a special point scheme for $\Omega_{\vec{r}'}$. The scheme involves choosing a set of values for $\Omega_{\vec{r}'}$ at random but at fixed relative positions and uses the summation over the values of $\psi(R)$ at these special points (with appropriate weighting factors) to obtain an unbiased estimator of the integral. The procedure for generating special points for different angular momenta is straightforward and is discussed in Ref. 16. With this scheme, the computational effort involved in the nonlocal energy calculation is quite manageable and is comparable to that for the kinetic energy.

3. Application to Solids and Atoms

We present in this section several applications of the present approach to atoms and solids. Results on binding energies and structural properties as well as those on the single-particle properties are discussed.

3.1. Binding Energies and Structural Properties

Atoms. The total energy, ionization potential, and electron affinity of atoms have been determined. These results were obtained by carrying out calculations for the ground-state energy of the neutral, positively, and negatively charged atoms. In each case, we used the cups condition to fix the parameter a in the expression (Eq. (4)) for the two-body term $u(r_{ij})$ in the Jastrow factor and searched the b, α parameter space to determine the optimal u and X functions to minimize the total energy. Note that since the atoms are spin-polarized (neglecting spin-orbit interactions), Eq. (5) gives a different X function

TABLE I. Ionizational energy and electron affinity of atomic carbon and silicon (in eV). The expected statistical error in the last digits is in parentheses.

	Variational QMC	Experimental[a]
Carbon		
Ionization Energy	11.43(5)	11.26
Electron Affinity	1.05(10)	1.27
Silicon		
Ionization Energy	8.20(5)	8.15
Electron Affinity	1.20(10)	1.39

[a] Ref. 19.

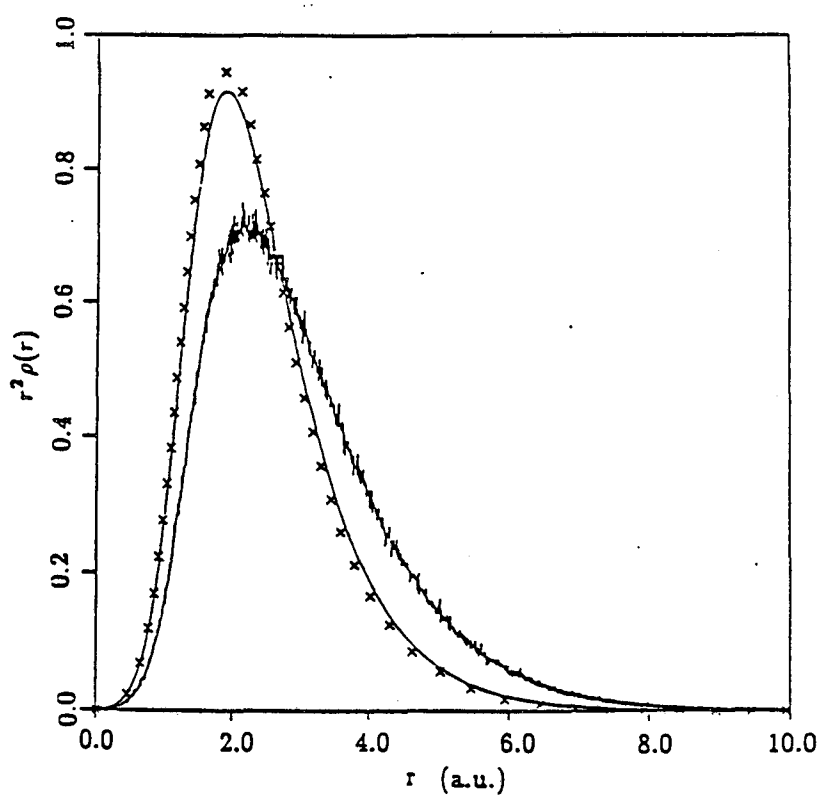

Fig. 1. Calculated valence electron charge density of carbon atom. The solid line is the LDA calculated result; the jagged curve is the QMC result with the two-body term $u(r_{ij})$ only in the Jastrow factor; the crosses are QMC results calculated with both the one- and two-body terms [$\chi(\vec{r}_i)$ and $u(r_{ij})$] included in the Jastrow factor (see text).

for different spin components.

The computed values for the ionization energy and electron affinity of atomic carbon and silicon are presented in Table I together with the experimental values. The agreement between theory and experiment is quite good (both C^- and Si^- are unbounded in the LDA). We find that both the one-body and two-body terms in the Jastrow factor are important to obtain quantitative results in the present approach. Without inclusion of the one-body term X, the presence of a nonzero $u(r_{ij})$ significantly alters the charge density from that of the Slater determinant alone. (See Fig. 1.) Because $u(r_{ij})$ is a two-body correlation term, it has the effect of reducing the electron density in the high-density regions and increasing it in the low-density regions. The resulting electron density is, in fact, too diffuse as compared to experiment. The inclusion of a X term as given in Eqs. (5) and (6) relaxes the electron distribution to one very similar to that of the LDA and lowers the total energy. For neutral carbon, the one-body term further lowered the total energy by 1.8 eV.

We note that the form of the wavefunction in Eq. (2) neglects three-body and higher order terms in the Jastrow factor. Since the number of three-body interactions is very different for C and Si in the three different charge states, the results in Table I suggest that three-body terms in the Jastrow factor appear to be not very significant in this case. Furthermore, the variational QMC results not only gives the relative energies for the various ionization states correctly. It also gives the absolute energies quite accurately at least for the case of the Si atom where our results may be compared to a recent Green's function QMC calculation using a pseudo-Hamiltonian formalism.[17] The Green's function QMC result for the total valence electron energy is -103.57(3) eV, which is only - 0.1 eV lower than our result of -103.42(5) eV for the neutral Si atom.

Solids. The approach has been applied to study carbon- and silicon-based crystals. Simulation cells with periodic boundary condition containing up to N = 216 electrons (or 54 atoms) were used. We find that, with this size simulation cell, the many-electron part of the energy is well converged. Finite size scaling to the final $N \to \infty$ limit is primarily dominated by the one-electron terms which are dependent on the k-point sampling in the Brillouin zone. (A fine grid in k-space is equivalent to a large simulation cell in real space.)

The result for diamond is summarized in Fig. 2. The total energy per carbon atom in the diamond crystal structure is calculated as a function of the lattice constant and fitted with a Murnaghan equation of state. We obtained a calculated equilibrium lattice constant of 3.54 ± 0.03 Å and a bulk modulus of 420 ± 50 GPa in good agreement with experimental values of 3.567 Å and 443 GPa, respectively[18]. Similarly accurate results for these structural parameters have been obtained for the case of silicon.

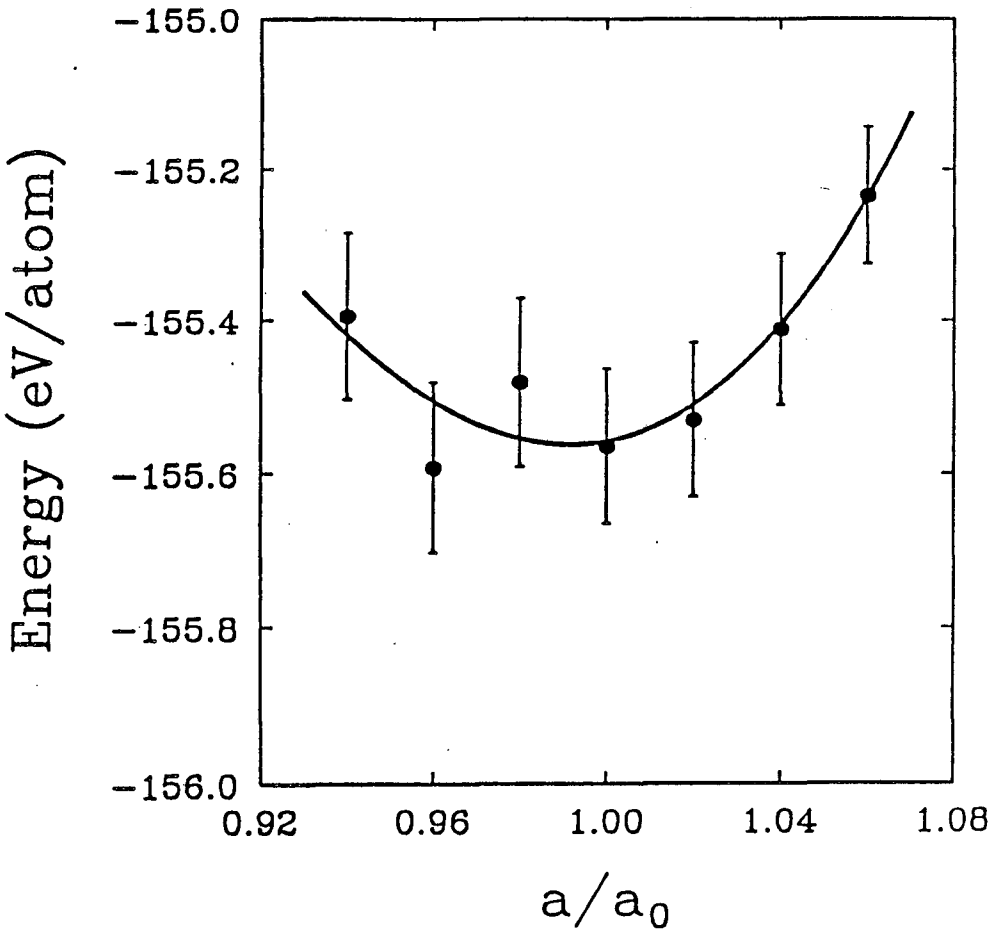

Fig. 2. Calculated total energy of diamond as a function of the ratio of the lattice constant a to the measured lattice constant a_0. The curve is a fit of the Murnaghan equation of state to the calculated points. The error bars indicate the standard deviation of the mean in each Monte Carlo calculation.

TABLE II. Calculated cohesive energies (in eV).

	Theory	Experiment[a]
Diamond	7.45(7)	7.37
Graphite	7.42(7)	7.39
Silicon	5.13(7)	4.62-4.97[b]

a) Ref. 19
b) Ref. 20

The calculated cohesive energies for the crystals diamond, graphite and Si are presented in Table II. In obtaining theoretical values, we have included the zero-point energy of the phonons in the energy of the solid. As can be seen from the Table, the present results are in excellent agreement with experiment[19,20]. In general, Hartree-Fock calculations significantly underestimate the cohesive energy whereas the LDA calculations tend to overestimate the cohesive energy of crystals, typically by 15-20%. This is illustrated in Table III for the case of diamond. Also from Table III, we see that when the one- and two-body terms are included in the Jastrow factor, the correlation energies for the valence electrons in the atom and the diamond crystal are 2.4 ± 0.1 eV and 4.1 ± 0.2 eV, respectively. Thus electron correlation effects play a very important role in determining the crystalline cohesive energy. The present values of the correlation energies for the carbon valence electrons are in agreement with results from a recent calculation using a similar Ansatz for the many-electron wavefunction, but evaluating the energy by diagrammatic techniques[1].

3.2. Single-Particle Properties

Information on some of the single-particle properties of the ground-state system may be obtained from the simulation. The simplest of these to evaluate is the single-particle orbital occupation number

$$n_\phi = \langle\psi|C_\phi^\dagger C_\phi|\psi\rangle \tag{12}$$

where $\phi(\vec{r})$ corresponds to some single-particle wavefunction. In the first quantized form,

$$[C_\phi\psi](\vec{r}_2, \vec{r}_3, \ldots, \vec{r}_N) = \int \phi^*(\vec{r}_1)\psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)d\vec{r}_1 \tag{13}$$

and thus n_ϕ may be easily evaluated in the Monte Carlo walk. Similarly the momentum distribution $n_{\vec{k}}$ is the occupation number for the planewave orbitals.

Figure 3 shows the calculated n_ϕ for the various LDA single-particle band (or Kohn-Sham) orbitals that go into our Slater determinant for the case of diamond. Owing to electron correlations, n_ϕ is reduced, as expected, from the independent particle value of $n_\phi = 2$ for states below the valence band maximum (vbm). This deviation is on the order of a few percent.

From the ground-state wavefunction, it is also rather straightforward to obtain the pair correlation function $g_{\alpha\beta}(\vec{r}_1,\vec{r}_2)$ through the usual relation

$$g(x_1,x_2)n(x_1)n(x_2) = N(N-1)\int |\psi(r_1 = x_1, r_2 = x_2, \ldots, r_N)|^2\, dr_3 \ldots dr_N \tag{14}$$

where n is the electron number density and spin indices are suppressed. Our results for $g_{\alpha\beta}(\vec{r}_1,\vec{r}_2)$ of diamond and silicon showed that,

TABLE III. Total energies (in eV/atom) of the carbon atom and of diamond (with finite-size correction) for (a) LDA calculation, and for Monte Carlo calculations with (b) single Slater determinant of LDA wavefunctions and (c) Jastrow-Slater function with one- and two-body terms in the Jastrow factor. The expected statistical error in the last digits is in parentheses.

	Carbon Atom E_{tot}	Diamond E_{tot}	Cohesive Energy
(a) LDA	-146.79	-155.42	8.63
(b) Slater Det.	-145.55(7)	-151.3(2)	5.85(25)
(c) Jastrow-Slater	-147.93(3)	-155.38(6)	7.45(7)
(d) Experiment[a]	---	---	7.37

a) Ref. 19.

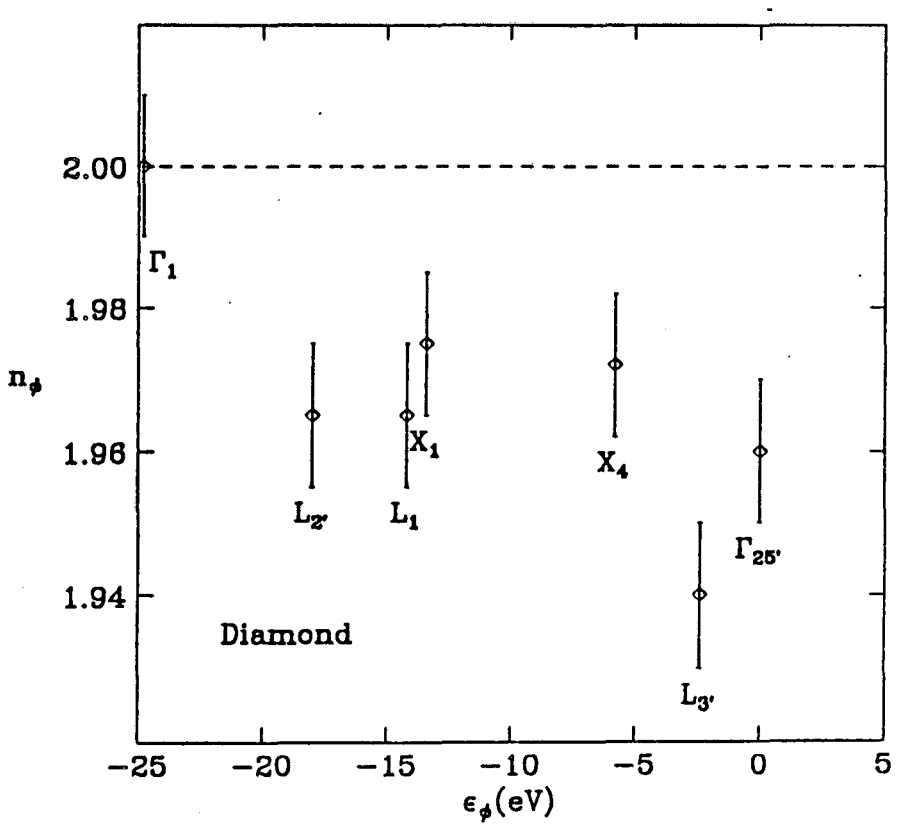

Fig. 3. Calculated single-particle orbital occupancy as a function of the energy of the various LDA Kohn-Sham orbitals.

unlike the uniform electron gas case, g is indeed highly anisotropic and is a sensitive funciton of both $\vec{r}_1$ and $\vec{r}_2$ separately. In particular we find that $g_{\uparrow\downarrow}$ is very rich in structure. For example, the correlation hole, $h^b_{\uparrow\downarrow}(\vec{r}) = g_{\uparrow\downarrow}(\vec{r}_1,\vec{r}) - 1/2$, for $\vec{r}_1$ located at the bond center has a density distribution which is distinctly related to the structure and covalent character of these materials. $h^b_{\uparrow\downarrow}(\vec{r})$ is negative near $\vec{r}_1$ the bond center as expected but $h^b_{\uparrow\downarrow}(\vec{r})$ is positive only in the nearby low density antibonding/interstitial regions and not in the neighboring bond centers.

Finally we have carried out calculations to estimate the quasiparticle excitation energy of a system by considering the difference in energy between a system in the ground state with that of a system with an added hole. By assuming that our variational wavefunction is a sufficiently accurate approximation for the true gound-state wavefunction, the quasihole energy may be expressed as

$$\varepsilon_\phi = E^*_{N-1} - E^o_N = \frac{\langle\psi|C^\dagger_\phi H C_\phi|\psi\rangle}{\langle\psi|C^\dagger_\phi C_\phi\psi\rangle} - \langle\psi|H|\psi\rangle$$

$$= \frac{\langle\psi|C^\dagger_\phi[H,C_\phi]|\psi\rangle}{\langle\psi|C^\dagger_\phi C_\phi|\psi\rangle} \qquad (15)$$

where ϕ corresponds to a quasihole wavefunction. In our calculation for diamond, we used the LDA wavefunction for ϕ [21]. Our preliminary results show quite good agreement with experiment (e.g. a bandwidth of 24.9 ± 1 eV for diamond as compared to the experimental value of 21-24 eV) and with other calculations[22,23]. However, the present scheme can only be considered as a way of obtaining an upperbound for the excitation energy since Eq. (15) in fact rigorously gives the first moment of the spectral function $A_\phi(\omega)$ of the state $C_\phi|\psi\rangle$ and not the peak position in $A_\phi(\omega)$. For the case that a single quasiparticle peak is well-defined and dominant, Eq. (15) would give a good approximation for the quasiparticle energy as defined as the position of a well-defined peak in $A_\phi(\omega)$.

4. Summary

We have presented a new method of calculating the total energy and related properties of crystals using nonlocal pseudopotentials in conjunction with variational quantum Monte Carlo techniques. The approach employs a many-electron wavefunction of the Jastrow-Slater form. Calculations have been carried out successfully for the cohesive energy and structural properties of carbon- and silicon-based solids. With both a one-body and a two-body term in the Jastrow factor, it is found that the approach can yield up to 95% of the electron correlation energy in the systems studied. Calculations have also been carried out to compute the single-particle orbital occupancy, electron pair-correlation functions, and quasiparticle excitation energies. These quanti-

ties are not accessible in standard self-consistent field approaches such as the density function formalism.

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