Variational Quantum Monte Carlo Nonlocal Pseudopotential Approach to Solids: Cohesive and Structural Properties of Diamond

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A new method of calculating total energies of solids which uses nonlocal pseudopotentials in conjunction with the variational quantum Monte Carlo approach is presented. By use of pseudopotentials, the large fluctuations of the energies in the core region of the atoms which occur in quantum Monte Carlo all-electron calculations are avoided. The method is applied to calculate the binding energy and structural properties of diamond. The results are in excellent agreement with experiment.

In this Letter, we present a new method of performing quantum Monte Carlo (QMC) calculations for solids and atoms using nonlocal pseudopotentials, thus extending the range of practical applicability of the QMC method for many-fermion systems for the first time to real solid-state systems involving heavier $(Z > 2)$ elements. This approach is used to calculate the correlation energy and structural parameters of diamond. The lattice constant is within 1% of the experimental value. The calculated cohesive energy is 7.45 ± 0.07 eV/atom, as compared to the experimental value of 7.37 eV/atom. This result is thus in significantly better agreement with experiment than the value of 8.63 eV/atom for the binding energy of diamond obtained with the local-density-functional formalism. Typically, local-density-approximation (LDA) binding energies are too large by 15%-20%.

The variational Monte Carlo method, as applied to quantum-mechanical many-body problems, was pioneered by McMillan[1] to study liquid ^{4}He and first applied to fermion-liquid problems by Ceperley, Chester, and Kalos.[2] More recently, the Green's-function quantum Monte Carlo approach to the many-electron problem has been applied very successfully to the electron gas,[3] to light molecules,[4] and to solid hydrogen.[5] However, a straightforward application of the method to real materials containing heavier atoms has been severely hampered by the very rapid growth in the required computation time with increasing atomic number.[6] This growth is caused primarily by the fluctuations in the energies of electrons in the core region. The motivation to overcome this restriction on quantum many-body calculations is high, especially for strongly correlated electronic systems with d and f electrons that are of major current interest and importance. Even in condensed-matter systems where the electronic structure can be said to be reasonably well understood, the standard approach of local-density-functional theory[7] has consistently failed to give correct binding energies,[8] although other

structural properties may be in good agreement with experiment.

A natural first step towards a full many-body theory of both strongly and weakly correlated electronic systems is the variational QMC approach. The desire to study a wider class of real condensed-matter systems has prompted our development of a pseudopotential approach, which replaces the effects of the core electrons by an ionic potential. This has proven very successful[9] in the treatment of many systems within local-density-functional theory. The ionic pseudopotentials used are those generated by the scheme of Hamann, Schlüter, and Chiang[10] for LDA calculations.[7] The nonlocality of the pseudopotential makes the present problem different from previously considered QMC problems. However, this problem can be overcome in the variational QMC method. In the Green's-function QMC approach[3,4] a nonlocal potential causes much greater problems because the propagator is not positive definite and only transient estimates of averages can be obtained.

In the present approach, as in other variational calculations for ground-state energies, we choose a correlated *trial* wave function and evaluate the expectation value of the *exact* Hamiltonian for this wave function. The many-body integrals are evaluated with the Metropolis Monte Carlo algorithm[11] for importance sampling. The importance function is $|\Psi(R)|^2$, the square modulus of the many-body wave function at the configuration $R \equiv \{r_i\}_{i=1}^N$. Thus, the random walk proceeds so as to visit points R in configuration space with probability density equal to $|\Psi(R)|^2$. The average of a quantity over the walk is an unbiased estimator of the integral of the quantity with respect to the weight $|\Psi(R)|^2$:

$$\int f(R) |\Psi(R)|^2 dR \simeq \frac{1}{n} \sum_{i=1}^n f(R_i). \quad (1)$$

For the total energy, the function $f(R)$ is taken to be $[H\Psi](R)/\Psi(R)$.

As the trial many-body wave function we use the

Jastrow-Slater form[2]:

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

where D is a Slater determinant of single-particle wave functions. In the present application to diamond, we will use the LDA single-particle wave functions.[12] In systems where the LDA fails more drastically than in diamond, a different approach to the choice of single-particle wave functions may be necessary. The many-electron Hamiltonian,

$$H = \sum_{i=1}^{N}\left\{-\frac{\hbar^2}{2m}\nabla_i^2 + V_{\text{ext}}(\mathbf{r}_i) + \frac{1}{2}\sum_{j\neq i}\frac{e^2}{r_{ij}}\right\}, \tag{3}$$

consists of the usual three terms: the kinetic energy of the valence electrons, an external potential (due to the ions in the crystal), and the Coulomb interaction between the valence electrons. In the present calculation, the kinetic and electron-electron energies are evaluated as in Ref. 2. The value of the local part of the external potential at each configuration on the random walk is evaluated with Ewald summation techniques.

The nonlocal part of the external potential involves the evaluation of the many-body wave function on a sphere about each atom. The nonlocal potential for an ion at the origin acting on the ith electron has the form[10]

$$H^i_{\text{nonlocal}} = \sum_l \int_0^{\infty} dr\, V_l(r)P^i_{l,r}. \tag{4}$$

Here $P^i_{l,r}$ is the angular momentum l projection operator. For a given configuration $\{\mathbf{r}_j\}_{j=1}^{N}$, with $\mathbf{r}_i = \mathbf{r}$, the contribution from the angular momentum potential $V_l(r)$ to the energy is

$$E^j(\mathbf{r}_1,\ldots,\mathbf{r}_i=\mathbf{r},\ldots,\mathbf{r}_N) = V_l(r)Y_{l0}(0,0)\int_{r'=r}Y_{l0}^*(\Omega_{r'})\frac{\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_i=\mathbf{r}',\ldots,\mathbf{r}_N)}{\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_i=\mathbf{r},\ldots,\mathbf{r}_N)}d\Omega_{r'}, \tag{5}$$

where $\Omega_{r'}$ is the angular coordinate of the vector $\mathbf{r}'$ when $\mathbf{r}$ points along the polar axis. The nonlocal potentials are very short ranged ($\simeq 2$ atomic units)[10] and so we need only sum the potentials of at most two neighboring atoms. In the present application the nonlocal potential has only an s component. For the s-projection operator we take the integral in Eq. (5) as the average of the integrand at four points $(\pi/2\pm\theta,\phi\pm\pi/2)$ with equal weight. The point $\Omega_1 = (\pi/2+\theta,\phi+\pi/2)$ is chosen randomly at each step with a uniform solid-angle distribution. This estimator is unbiased for all functions and has zero variance for projection of s and p functions. We will discuss the procedure for generating special points for higher angular momenta in a longer paper.[13] The computational effort involved in the evaluation of the nonlocal potential with this scheme is comparable to that for the kinetic energy.

We have applied the method to study the binding energy and equilibrium lattice constant of diamond. A simulation supercell containing 16 atoms (or 64 electrons) in the diamond structure with periodic boundary conditions was used. For some calculations, a larger region containing 54 atoms (or 216 electrons) was used to determine finite-size effects. The size dependence for larger simulations is mainly determined by the convergence of the one-body terms, as given within band theory by the k-point sampling of the Brillouin zone.

The function $u(r_{ij})$ in the Jastrow factor is chosen for the solid to be of the standard form $u(r) = A(1-e^{-r/F})/r$. The value of A (and the asymptotic $1/r$ dependence) is determined by the zero-point motion of the plasmons in the solid, as discussed in previous work on the uniform electron gas.[14] The value of F is different for like and unlike spins and is chosen to satisfy the "cusp" condition[14] on $u(r)$, due to the singularity of the Coulomb interaction, as $r\rightarrow 0$. Although these conditions on $u(r)$ do not determine its optimal form in the intermediate region ($r\sim r_s$), we have found, by relaxing these conditions on A and F and by adding an intermediate-range term, $C\exp[-(r/r_s)^2]$, to u that in practice these values of A and F (and the original form of u) are at the variational minima within statistical noise. In the atom, $u(r_{ij})$ is chosen to be of the form[4] $u(r) = -ar/(1+br)$. The cusp condition on $u(r)$ as $r\rightarrow 0$ still applies in the atom and is used to determine a. The value of b is found by minimizing the energy with respect to this parameter. We have also used the same form of u in the atom as for the solid, with identical results. For the one-body term in the Jastrow factor, we set $\chi(\mathbf{r}) = \alpha\ln[\rho_{\chi,u=0}(\mathbf{r})/\rho_{\chi=0}(\mathbf{r})]/2$, where $\rho(\mathbf{r})$ is the charge density and α is a variational parameter. The optimum value of α is close to 1, as expected, since the LDA charge density is generally quite good. This approach gives values for the ionization energy and electron affinity of carbon in agreement with experiment within ± 0.2 eV/atom (C^- is unbound in LDA).[13] It appears then that three-body terms in the Jastrow factor can only lower the energy by no more than approximately 0.2 eV/atom.

As is shown in Table I, the introduction of a Jastrow factor with only the two-body term u lowers the total energy of the solid by approximately 3.8 eV/atom. With the introduction of the Jastrow factor, the electron-

TABLE I. Terms in the total energy of the solid (64-electron simulation at a lattice constant $a = 3.63$ Å) for a single Slater determinant of LDA wave functions and for a Jastrow-Slater function with a two-body term *only* in the Jastrow factor, as discussed in the text, and with LDA wave functions in the determinant. Energies in eV/atom.

	Slater determinant	Jastrow-Slater (u only)
Local potential	−87.1	−73.6
Electron-electron	−29.2	−39.0
Kinetic	121.3	116.8
Nonlocal potential	15.8	12.8
Ewald sum	−171.0	−171.0
Total	−150.2	−154.0

TABLE II. Total energies (in eV/atom) of the carbon pseudoatom and of diamond (with finite-size correction) for (a) LDA calculation, and for Monte Carlo calculations with (b) single Slater determinant of LDA wave functions 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	Diamond	Cohesive energy
(a) LDA	−146.79	−155.42	8.63
(b) Slater determinant	−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]See Ref. 12.

electron energy is substantially reduced. However, the kinetic energy also decreases, contrary to our experience with uniform systems; it is the electron-ion energy (local plus nonlocal potential terms) which is greatly increased. The general trends in the atom are similar. In that case the introduction of u lowers the total energy of the pseudoatom by approximately 0.6 eV. Without the one-body term $\chi(r)$ in the Jastrow factor, the presence of a nonzero $u(r_{ij})$ alters the charge density from that of the Slater determinant alone. Because $u(r)$ is a decreasing function of r, its effect is to reduce the charge density in the high-density regions and increase it in the low-density regions. This explains both the increase in the electron-ion energy and the decrease in the kinetic energy.

With the introduction of the one-body term in the Jastrow factor, the energy of the solid is further reduced by 0.3 eV/atom. In the atom the one-body term is more important, lowering the energy by 1.8 eV. In systems where the LDA charge density is poor, a different approach to the χ factor would be necessary. It is possible to derive, subject to certain approximations, an Euler-Lagrange equation for χ to minimize the energy.[13] In principle, this allows us to determine χ entirely within the QMC approach.

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 solid are thus found to be 2.4 ± 0.1 eV and 4.1 ± 0.2 eV/atom, respectively. This is in reasonable agreement with recent calculations[15] for the valence electrons in an all-electron calculation using a similar *Ansatz* for the many-body wave function, but evaluating the energy by diagrammatic techniques. The estimate of the Hartree-Fock binding energy obtained with LDA wave functions in a single Slater determinant is 5.85 ± 0.25 eV/atom, in agreement with the results of Ref. 15.

The final results for the binding energy of diamond in the present approach are shown in Table II and compared with the LDA results using the Ceperley-Alder

form for the exchange-correlation energy.[16] We have included the zero-point energy of the phonons in the energy for the solid. The Monte Carlo calculation gives a binding energy of 7.45 ± 0.07 eV/atom, in excellent agreement with the measured value of 7.37 eV/atom.[12] The results obtained from the QMC calculations of the energy as a function of lattice constant are fitted with a Murnaghan equation of state, as shown in Fig. 1. We obtain a fitted equilibrium lattice constant of 3.54 ± 0.03 Å and bulk modulus of 420 ± 50 GPa, compared with experimental values of 3.567 Å and 443 GPa, respectively.[12]

In conclusion, we have performed variational quantum Monte Carlo calculations of the binding energy, equilib-
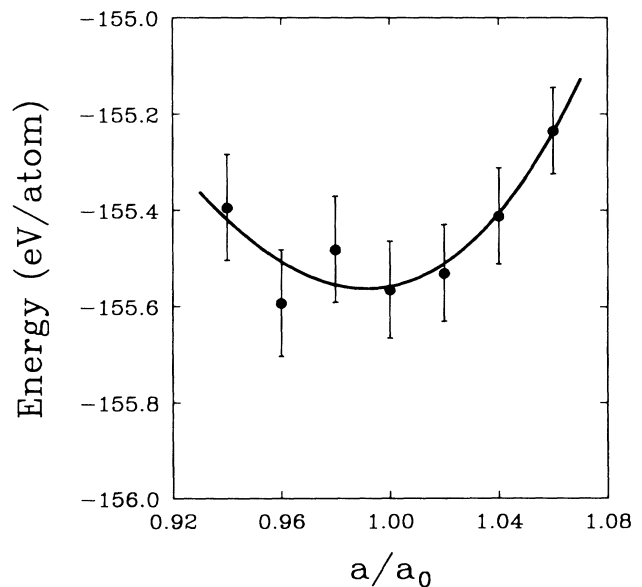

FIG. 1. Calculated total energy of diamond as a function of the ratio of the lattice constant to the measured lattice constant. The curve is a fit of the Murnaghan equation of state to the calculated points. The error bars indicate the standard deviation of the mean in each Monte Carlo calculation.

rium lattice constant, and bulk modulus of a solid, using nonlocal pseudopotentials. We demonstrated the computational feasibility of the method and obtained results in excellent agreement with experiment for both the cohesive energy and structural properties of diamond. It should be straightforward to apply the method to many other materials, including the d-band metals and other strongly correlated electron systems, where the LDA has had more serious problems. It is also possible to examine quantities which are not accessible in the LDA approach, such as explicit pair correlation functions and many-body effects on Compton profiles.

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