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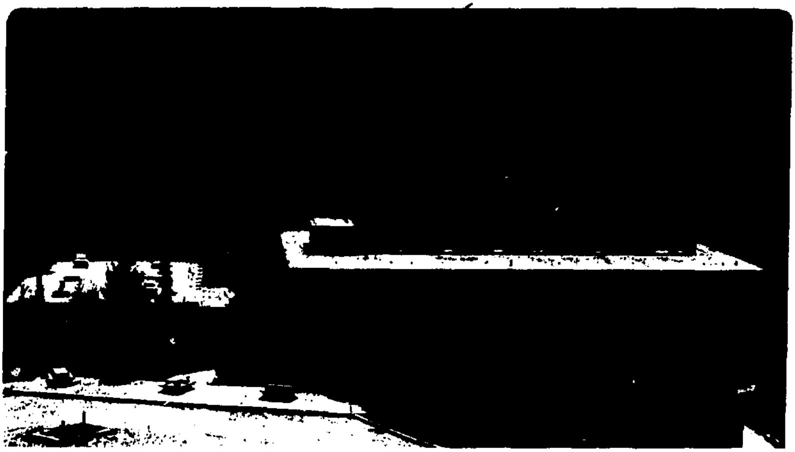

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QUANTUM MONTE CARLO CALCULATION OF THE PROPERTIES OF ATOMIC CARBON AND DIAMOND

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A new method of calculating total energies of solids using non-local pseudopotentials in conjunction with the variational quantum Monte Carlo approach is presented. By using pseudopotentials, the large fluctuations of the energies in the core region of the atoms which occur in quantum Monte Carlo all-electron schemes are avoided. The method is applied to calculate the cohesive energy and structural properties of diamond and the first ionization energy and electron affinity of the carbon atom. The results are in excellent agreement with experiment.

A natural first step towards a full many-body theory of both strongly and weakly correlated electronic systems is the variational quantum Monte Carlo (QMC) approach. However, a straightforward application of the method to the electronic properties of real materials containing heavier atoms has been severely hampered by the very rapid growth in the required computation time with increasing atomic number[1]. The growth is caused primarily by the fluctuations in the energies of electrons in the core region. This problem has prompted our development of a quantum Monte Carlo pseudopotential approach[2], which incorporates the effects of the core electrons in an ionic potential. The ionic pseudopotentials used are those generated[3] for local density-functional (LDA) calculations. The integral operator which arises in the non-local pseudopotential[3] makes the present problem different from previously considered QMC problems. However, this operator can be evaluated statistically within the variational QMC method with a computational effort comparable to that for the kinetic energy[2].

In the present approach, we choose a correlated *trial* wavefunction for the valence electrons of the form:

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

where D is a Slater determinant of single-particle wavefunctions. We will use the LDA single-particle wavefunctions[4]. For this wavefunction we evaluate the expectation value of the *exact* many-body Hamiltonian for the valence electrons in an external potential due to the ions. In the present calculation, the kinetic and electron-electron energies are evaluated as in Ref. 5. The external potential is the sum of the ionic pseudopotentials which have a local and a (short-ranged) non-local part. The many-body integrals are evaluated using the Metropolis Monte Carlo algorithm[6] for importance sampling.

The two-body correlation term, $u(r_{ij})$, in the Jastrow factor lowers the energy by reducing the probability of two electrons coming close together. In the solid, $u(r_{ij})$ is chosen to be of the standard form[7], $u(r) = A(1 - e^{-r/F})/r$. In the atom, $u(r) = -ar/(1 + br)$. The variational parameters, A and F in solids and a in atoms may be fixed by physical constraints[2]. We set $\chi(\mathrm{r}) = \alpha \log[\rho_{\chi,u=0}(\mathrm{r})/\rho_{\chi=0}(\mathrm{r})]/2$, where $\rho(\mathrm{r})$ 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.

We have applied the method to study the cohesive 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 determined almost entirely by the convergence of the one-body terms, as given within band theory by the k-point sampling of the Brillouin zone.

We have performed calculations for $C(^3P)$, $C^+(^1P)$, and $C^-(^4P)$. In each case, the b,α parameter space was searched to determine the optimal parameters. Since the atoms are spin-polarized, we have used different χ-functions for different spin types, although for reasons of simplicity we have kept a single variational parameter α. The calculation was repeated for C and C^+ using the same form of u as in the solid. Both forms of u give essentially the same total energies for each system.

The correlation energies for the valence electrons in the atom and the solid are found to be 2.4 ± 0.1 eV and 4.1 ± 0.2 eV/atom, respectively. This is in reasonable agreement with recent calculations of Stollhoff and Bohnen[8] for the valence electrons in an all-electron calculation using a similar ansatz for the many-body wavefunction but evaluating the energy by perturbation techniques. The value of the Hartree-Fock cohesive energy obtained using LDA wavefunctions in a single Slater determinant is 5.85 ± 0.25 eV/atom, in agreement with the results of Ref. 8.

Table I. Correlation energy contributions to electron affinity and first ionization potential (in eV). Statistical error in the last digits is in parentheses.

	E. A.	1st I. P.
LDA	C^- unbound	0.97
QMC	0.67(5)	0.57(5)
Expt.	0.72	0.47

Table II. Total energies (in eV/atom) for (a) LDA, (b) Monte Carlo with single Slater determinant, (c) with Jastrow function and a Slater determinant, and for experiment.

	Carbon Atom	Diamond	Cohesive
Theory:			
(a)	-146.79	-155.42	8.63
(b)	-145.55(7)	-151.3(2)	5.85(25)
(c)	-147.93(3)	-155.38(6)	7.45(7)
Expt.	—	—	7.37

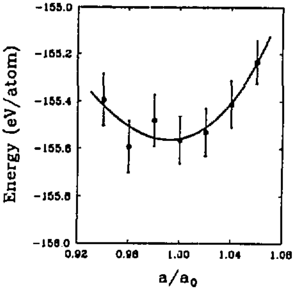

Figure 1 : Calculated total energy of diamond as a function of the ratio of the lattice constant to the measured lattice constant. The error bars indicate the standard deviation of the mean in each QMC calculation.

The calculated correlation energy contributions to the electron affinity and the first ionization potential of carbon, together with LDA results and experimental values, are presented in Table I. The improvement over LDA results is very sizable and the agreement with experiment is good. (The LDA result quoted is the difference between the first ionization potential obtained from LDA and that from Hartree-Fock.)

The final results for the cohesive energy of diamond in the present approach are shown in Table II and compared with the LDA results. The QMC value for the cohesive energy is in excellent agreement with experiment, in contrast to the overbinding of 1.26 eV/atom in LDA. The results obtained from the QMC calculations of the energy as a function of lattice constant are fitted to 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[4].

In conclusion, we have performed variational quantum Monte Carlo calculations of the cohesive energy, lattice constant, and bulk modulus of a solid and the first ionization potential and electron affinity of an atom, using non-local pseudopotentials. We demonstrated the computational feasibility of the method and obtained results in excellent agreement with experiment for diamond and for atomic carbon. The method opens the possibility of performing variational quantum Monte Carlo calculations for the valence electrons of solids and atoms involving elements beyond the first row of the Periodic Table.

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