

Cohesive energy of silicon by the Green's-function Monte Carlo method

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The total energy of diamond-structure silicon is calculated by a fixed-node Green's-function Monte Carlo method using a pseudo-Hamiltonian to eliminate the core electrons. This demonstrates the feasibility of calculating properties of solids with the quantum Monte Carlo method, since the statistical error for a supercell of 64 atoms is < 0.02 eV/atom. The agreement with experiment, although good, is limited by the accuracy of the pseudo-Hamiltonian. We find that the correlation energy is improved over a variational pair-product trial function by 0.34 eV/atom in the solid compared with 0.21 eV in the free atom.

Green's-function Monte Carlo (GFMC) methods can, in principle, be used to calculate exact properties of many-body systems.¹ In practice, very accurate results have been obtained for simple systems like the homogeneous electron gas,² light molecules,³ and solid hydrogen.⁴ Such methods have never been applied to a real solid heavier than lithium, however, because the presence of core electrons introduces large fluctuations in the energies and thereby reduces the computational efficiency. Recently, Fahy, Wang, and Louie⁵ applied a variational Monte Carlo (VMC) method to Si and C by using nonlocal pseudopotentials (PP) to avoid core electrons. In the present work we present GFMC calculations on Si, which start from VMC trial functions of the same form as in Ref. 5, and project out the lowest possible upper bound for the ground-state energy, within the "fixed-node" constraint, i.e., that the $(3N-1)$ -dimensional nodal surface of the wave function is assumed to be the same as in the VMC trial function. We expect our results to be close to the exact energy for the assumed Hamiltonian since the error due to the fixed-node constraint has been calculated in cases such as the electron gas² and Si atom and molecules.⁶ The resulting structural properties and cohesive energy of silicon are in good agreement with experiment considering the method used to eliminate the core electrons is based on a mean-field theory.

It was shown⁶ that a nonlocal pseudopotential used within a fixed-node calculation will not necessarily be above the exact ground-state energy and the nonlocality will further complicate the random-walk algorithm. Bachelet, Ceperley, and Chiochetti⁶ constructed a local Hamiltonian with position-dependent masses (pseudo-Hamiltonian, or PH) and showed that it can accurately account for much of the angular momentum dependence of the pseudopotential for many atoms such as silicon.

The valence pseudo-Hamiltonian has the form:

$$H = - \sum_i \frac{\hbar^2}{2m} \nabla_i^2 + \sum_{i,I} h_I(\mathbf{r}_{iI}) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{r_{ij}} + \frac{1}{2} \sum_{I \neq J} \frac{(Ze)^2}{R_{IJ}}, \quad (1)$$

where ions of charge $Z=4$ are denoted by I, J , electrons by i, j , and \mathbf{r}_{ij} , \mathbf{r}_{iI} , and \mathbf{R}_{IJ} are relative positions. The effect of the core electrons is incorporated in the PH

$$h(r) = - \frac{\hbar^2}{2m} \nabla a(r) \nabla + \frac{b(r)}{2r^2} \mathbf{L}^2 + v(r), \quad (2)$$

where the functions $a(r)$, $b(r)$, and $v(r)$ are determined by the usual pseudopotential construction methods from atomic orbitals. Reference 6 compares energy levels of atoms and diatomics as calculated with the GFMC-PH with experimental and theoretical results. We have tested the accuracy of the PH in solid Si by comparing a local-density approximation⁷ (LDA) calculation of the PH and the PP (Ref. 8) from which the PH is constructed and find that the PH gives a binding energy at zero pressure 0.219 eV/atom higher than that of the PP, in agreement with Ref. 9. This difference increases with density and likely arises because the attractive d channel of the PP is not exactly reproduced in the PH. The PH could be improved to give better transferability in the d channel, but our initial attempts were not successful and we have used the PH from Ref. 6.

In GFMC (Ref. 10) the operator $\exp(-tH)$ projects out the ground state from the starting trial function which we choose to have the Jastrow-Slater form:

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \exp \left[\sum_{i=1}^N \chi(\mathbf{r}_i) - \sum_{i \leq j} u(\mathbf{r}_{ij}) \right] D(\mathbf{r}_1, \dots, \mathbf{r}_N), \quad (3)$$

where $u(r)$ is a two-body correlation function obtained from the random-phase approximation for a homogeneous electron gas;² $\chi(\mathbf{r})$ is a one-body term which modifies the VMC charge density and D is a Slater determinant of single-particle states calculated by LDA with plane-wave basis set. All reciprocal lattice vectors with an energy less than the “energy cutoff” are included. We have used two energy cutoffs (7 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. A release-node GFMC calculation for the atom shows that the difference in energy from the fixed-node GFMC is less than 0.01 eV while in the molecule it is less than 0.07 eV/atom with a much less accurate trial function than we used in the solid calculation. We estimate that the exact energy is lower than our fixed-node upper bound by less than 0.05 eV/atom in the solid. We have also tested that the GFMC energy is insensitive to changes in the other parts of the trial function.

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 quantum Monte Carlo (QMC) results are corrected assuming that they have the same size dependence as LDA has. We find that a system containing only 8 atoms is too small to represent bulk Si. The number of walkers in the GFMC ensemble is chosen to be 200. The initial distribution was obtained from VMC. A time step of 0.015 a.u. (this gives an acceptance ratio of 98% in the Metropolis portion of the time evolution) was used. A test calculation using half the time step gave identical results, showing that the time step error is less than 0.03 eV/atom. A typical run with 3×10^4 steps, took 20 h on a Cray-XMP.

Figure 1 shows the energy as a function of lattice constant from the LDA, VMC, and GFMC calculations. The curves are least-squares fits to the Murnaghan equation of state.¹¹ 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 probably because the atom has spherical symmetry rather than the weaker periodic symmetry of a lattice. In the solid, the energy drop monotonically increases with lattice constant, suggesting that the trial function of the form of Eq. (3) is slightly better at higher densities. 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

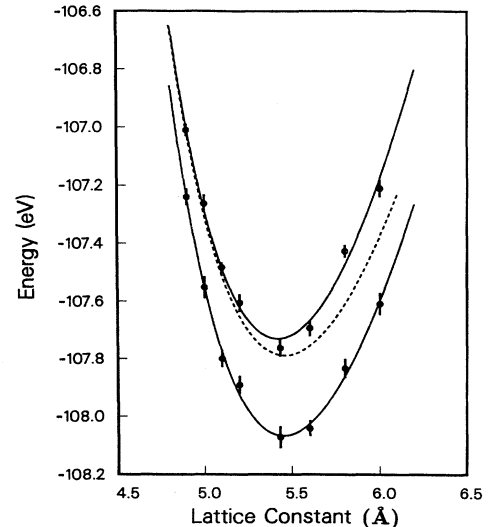


FIG. 1. Total energy of silicon vs lattice constant. The upper curve with error bars is from VMC and the lower from GFMC. Both have been corrected for the finite size of the system using LDA. The error bars show the estimated statistical errors. The solid lines are the fits to the Murnaghan equation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

from LDA are very close (~ 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.

It is known from the work on atoms and molecules and from Fahy, Wang, and Louie⁵ that the introduction of a Jastrow factor with *only* the two-body term u reduces the kinetic energy and the electron-electron energy, and increases the electron-ion energy. However, with the introduction of the one-body term χ in the Jastrow factor, the electron-ion energy is reduced, while the kinetic energy and the electron-electron energy are increased, as shown

TABLE I. Comparison of individual terms in the total energy of Si from (1) VMC with only the two-body term u in the Jastrow factor, (2) from VMC with both the two-body term u and the one-body term χ in the Jastrow factor, and (3) from GFMC. All numbers are from a 64 atom simulation in the diamond structure at a lattice constant $a=5.43$ Å and are in eV/atom. The GFMC mixed estimators have been corrected using the linear extrapolation method (Ref. 1); systematic errors due to higher-order terms are of order of 0.3 eV/atom for the first three lines but do not affect the total energy.

	VMC, u only	VMC, both u and χ	GFMC
Kinetic energy	39.31	40.26	40.78
External potential	-3.00	-5.30	-6.48
Electron-electron	-29.35	-28.43	-28.37
Ewald sum	-114.26	-114.26	-114.26
Total energy	-107.30	-107.72	-108.03

TABLE II. Comparison of the GFMC and VMC results with experiment and other calculations. All quantities have been corrected for finite-size effects and zero-point motion of the Si ions, but here there are no corrections applied to the difference between the pseudo-Hamiltonian and the pseudopotential.

	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(3)	-103.56(2)	-108.07(2)	4.51(3)
Expt.	5.430 ^c	0.992 ^d	3.20-4.68 ^e	· · ·	· · ·	4.63(8) ^f

^aOur calculation using the pseudopotential from Ref. 8 with an energy cutoff of 30 Ry.

^bReference 5.

^cAt $T=0$ K, Y. Okada and Y. Tokumaru, J. Appl. Phys. **56**, 314 (1984).

^dAt $T=0$ K, J. J. Hall, Phys. Rev. **161**, 756 (1967). It agrees with more recent results at room temperature.

^eLandolt-Börnstein: Numerical Data and Functional Relationships Science, edited by K.-H. Hellwege, New Series, Vol. 3, 17a (Springer, New York, 1982).

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in Table I. Therefore, the two-body term in the Jastrow factor over corrects the many-body wave function, and the effect of the one-body term is to correct it back. GFMC further reduces the electron-ion energy with respect to VMC (by 1.2 eV), while increasing the kinetic energy (by 0.5 eV). This shows that further improvements to the one-body term are possible.

The final comparison with experiment and other calculations is given in Table II. 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, Wang, and Louie. After correcting for the difference between the PH and PP as calculated by LDA, there is still a 0.2 eV difference. The trial functions used in the two calculations are essentially identical. We performed additional VMC calculations with their nonlocal 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). 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, Wang, and Louie. 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 agreement with the most quoted experimental value,^{12,13} 4.63(8) eV. In future work, we

will describe the results of GFMC calculations with a nonlocal potential using a method¹⁴ which treats the non-local parts in a variational manner.

In conclusion, we have applied the fixed-node Green's function Monte Carlo method to solid silicon using a pseudo-Hamiltonian to include the effects of core electrons. The main outcome of our work is simply to demonstrate that rigorous Monte Carlo calculations of solids are now possible, attaining an accuracy of 0.03 eV/atom and that the results are in good agreement with experiment. VMC works very well for a semiconductor like silicon, but to achieve an accuracy on the cohesive energy of better than 0.1 eV, GFMC is necessary. The uncertainty arising from the imperfect transferability of the LDA-derived pseudo-Hamiltonian is larger than the statistical errors, the fixed-node errors, and the finite system errors, all of which are smaller than 0.05 eV/atom. Applications to other materials where the pseudo-Hamiltonian is appropriate are in progress. We note that for future calculations, it is desirable to use a pseudo-Hamiltonian or pseudopotential derived from a many-body theory of the atom rather than from a mean-field theory like LDA.

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