

Quantum Monte Carlo Determination of Electronic and Structural Properties of Si_n Clusters ($n \leq 20$)

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Variational and fixed-node diffusion Monte Carlo methods are applied to study the structural and valence electronic properties of Si_n clusters. Binding energies for $n \leq 7$ agree within $\approx 4\%$ with experiments and within $\approx 2\%$ when the fixed-node error is decreased by using natural orbitals. For $n \geq 9$ we show that the local density approximation overbinds by $\approx 25\%$. We determined unambiguously (i) the role of correlation in the energy ordering for different structures, including our new lowest energy structure of Si_{20} , and (ii) a different ground state for Si_{13}^- than the one predicted by the local density approximation.

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The study of atomic clusters has become one of the most exciting areas of research because of the unique combination of molecular and condensed matter physics and the possibility of studying the transition from molecules to crystalline solids [1]. Recently, covalently bonded semiconductor clusters (such as C, Si, and Ge) have been given much attention [2–4] as they have rather different properties than the bulk materials and form unique structures which may be useful in generating new materials with novel and unusual properties [4,5]. In particular, Si_n clusters have been studied by both theoretical and experimental approaches [6–12], and for small n ground state structures have been identified [13] and very recently confirmed experimentally [14]. In spite of this effort, the situation is far from clear for larger clusters; e.g., a lower energy structure has just been found [15] for Si_9 . Except for the small clusters which were studied by quantum chemistry methods, most of the electronic structure calculations performed to date have used either empirical tight-binding models or local density approximation (LDA) approaches. While in most cases LDA provides excellent geometries and also a correct picture of the energy differences between structures with the same or similar number of atoms, one can expect a significant overbinding; in addition, it is not possible to assess the role of correlation energy in stabilizing a particular structure. This uncertainty in the correlation effect description has led, for example, to a controversy concerning the validity of LDA predictions regarding the stable structure of Si_{13} [11,16].

This Letter determines without ambiguity the impact of correlation on the structural and electronic properties of Si_n clusters using high-accuracy quantum Monte Carlo (QMC) methods. We find that the valence electron correlation energy per atom varies significantly from one structure to another even for larger clusters. We also evaluate the binding energies, which differ from available experiment by 2% to 5%, a significant improvement over the accuracy of LDA. For Si_{20} , a new elongated structure is proposed that

we find to be about 4 eV lower in energy than the dodecahedron, and about 2 eV lower than previously proposed elongated structures [12,17,18]. The ability of the QMC method to study effects which are very sensitive to an accurate description of correlation is illustrated by calculating the negative ion for the closed shell Si_{13} cluster, for which we find a different electronic ground state than LDA and evaluate the electron affinity to be 2.0(1) eV. Finally, we contribute to the development of the QMC method by addressing the fixed-node error as a significant source of the few percent discrepancy between our calculated binding energies and experiment. We show that the use of natural orbitals from correlated calculations instead of Hartree-Fock orbitals produces more accurate wave functions, decreasing the differences with experiment for the $n = 2, 3, 4$ cases to 1%–2%. To our knowledge, these QMC results represent the first *ab initio* many-body calculations of valence electronic structure for molecular systems with a large number of valence electrons.

In our QMC approach [19], we treat the core electrons with nonlocal pseudopotentials generated within Hartree-Fock theory [20] and use variational Monte Carlo (VMC) calculations to optimize the trial function $\psi_T(R)$, where R denotes coordinates of the valence electrons. In diffusion Monte Carlo (DMC) calculations, one simulates stochastically the imaginary time Schrödinger equation,

$$f(R, t + \tau) = \int G(R, R'; \tau) f(R', t) dR', \quad (1)$$

where $f(R, t) = \psi_T(R)\phi(R, t)$ and $G(R, R'; \tau)$ is a Green function which is known in the $\tau \rightarrow 0$ limit [21]. We treated the fermion antisymmetry problem by the commonly used fixed-node approximation [21], which restricts the nodes of $\phi(R, t)$ to be identical with the nodes of $\psi_T(R)$. The trial function used is a linear combination of Slater determinants of single electron spin-up and spin-down orbitals times a correlation factor [22,23],

$$\psi_T = \sum_n d_n D_n^\uparrow D_n^\downarrow \exp \left[\sum_{i,j} u(r_{i\uparrow}, r_{j\uparrow}, r_{ij}) \right], \quad (2)$$

where I corresponds to the ions, i, j to the electrons, and r_{il}, r_{jl}, r_{ij} to the distances. The Slater determinants are built from Hartree-Fock (HF) orbitals which are computed using the GAMESS package. Parametrization and optimization of $u(r_{il}, r_{jl}, r_{ij})$, which represents the electron-electron and electron-electron-ion correlations, are described elsewhere [24]. Within VMC the optimized $\psi_T(R)$ gave 85%–90% of the DMC correlation energy for all sizes of studied clusters.

Since the calculation of forces is not developed for QMC, searching and optimization of the structures is performed using LDA, which is well known to give excellent geometries. All structures are optimized within the given symmetries in order to have a direct comparison with previous calculations. A conjugate gradient as well as quasi Newton minimization are used, and atom positions are relaxed until forces become less than 0.003 a.u.

$n = 2$ to 7.—For these smaller clusters, the ground state structures were first determined theoretically by Raghavachari and Rohlfing [13] and recently confirmed experimentally through Raman spectroscopy [14], and thus provide an excellent test for the QMC approach. Table I lists our results for these clusters, as well as available experimental data. We are encouraged by the level of accuracy of the QMC results when compared with experiment [25] and point out that there is no decrease in accuracy with increased cluster size for $n = 4, 6, 7$. By contrast, LDA overbinding is 15%–20% for these small clusters, typical of errors found in LDA calculations [26].

$n = 9$ and 10.—For Si_9 the distorted tricapped octahedron is compared with a distorted tricapped prism (see Fig. 1) recently proposed by Ordejón, Lebedenko, and Menon [15]. For Si_{10} we study the tetracapped trigonal prism and the tetracapped octahedron. The total energies of these different geometries for each cluster size differed by less than 1 eV in previous calculations [13,15,27], and

TABLE I. Binding energies (eV/atom) calculated by the HF, LDA, and DMC methods compared with the available experimental data. HF and DMC valence atomic energies are -99.773 and $-102.121(3)$ eV, respectively.

	HF	LDA	DMC	Expt.
Si_2 (D_{2h})	0.85	1.98	1.580(7)	1.61(4)
Si_3 (C_{3v})	1.12	2.92	2.374(8)	2.45(6)
Si_4 (D_{2h})	1.61	3.50	2.86(2)	3.01(6)
Si_6 (C_{2v})	1.82	4.00	3.26(1)	3.42(4)
Si_7 (D_{5h})	1.91	4.14	3.43(2)	3.60(4)
Si_9 (C_s)	1.74	4.06	3.28(2)	...
Si_9 (D_{h3})	1.77	4.14	3.39(2)	...
Si_{10} (T_d)	1.94	4.25	3.44(2)	...
Si_{10} (C_{3v})	1.89	4.32	3.48(2)	...
Si_{13} (I_h)	1.41	3.98	3.12(2)	...
Si_{13} (C_{3v})	1.80	4.28	3.41(1)	...
Si_{13}^- (C_{3v})	1.88	4.43	3.56(1)	...
Si_{20} (I_h)	1.61	4.10	3.23(3)	...
Si_{20} (C_{3v})	1.55	4.28	3.43(3)	...

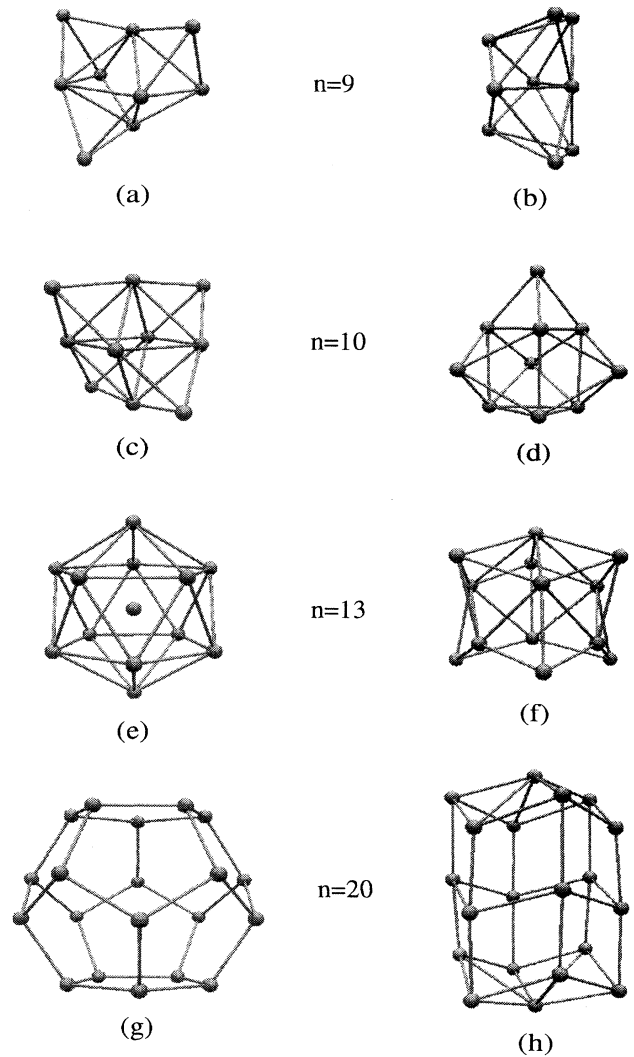


FIG. 1. Structures of calculated clusters for $n \geq 9$. (a) The 9-atom (C_s) distorted tricapped octahedron; (b) the 9-atom (D_{h3}) distorted tricapped prism; (c) the 10-atom (T_d) tetracapped octahedron; (d) the 10-atom (C_{3v}) tetracapped trigonal prism; (e) the 13-atom (I_h) icosahedron; (f) the 13-atom (C_{3v}) capped trigonal antiprism; (g) the 20-atom (I_h) dodecahedron; (h) the 20-atom (C_{3v}) new elongated structure.

it has not been clear which structure was more stable. Our results confirm the LDA and empirical tight-binding predictions in both cases, showing the distorted tricapped trigonal prism and the tetracapped trigonal prism to be lower in energy for Si_9 and Si_{10} , respectively.

$n = 13$.—These clusters are of interest because of the possibility of their having the high-symmetry icosahedral (I_h) geometry, which, for example, has recently been found to be a stable geometry for doped Al clusters [28]. However, a lower C_{3v} symmetry structure was found by a simulated annealing LDA search to be energetically more favorable for Si by about 0.5 eV/atom [11]. This led to the conjecture [16] that the electron correlation had not

been treated adequately and that proper calculations would show the icosahedron to be more stable. We calculated both structures, and for completeness three different occupations of the highest orbitals of the icosahedron are considered: A_g^2 singlet, G_g^2 singlet, and G_g^2 triplet. These possibilities come from the fact that Si_{13}^{++} (I_h) is a closed-shell molecule with the first two virtual orbitals (A_g and G_g) very near in energy. The two open-shell states of Si_{13} with double occupancy of the fourfold degenerate G_g orbital are essentially equal in energy, whereas the closed-shell A_g state is considerably higher, thus confirming the Jahn-Teller instability of the icosahedron as found in LDA [11]. We find indeed that the icosahedral structure has a larger correlation energy. It is not nearly enough, however, to overcome Coulomb and exchange contributions, and so the closed-shell C_{3v} structure is substantially lower in total energy.

$n = 20$.—In order to compare our results with recent calculations [12], we first considered the perfect dodecahedron structure even though it is not stable against Jahn-Teller distortion. We then went further and focused on a new structure for Si_{20} which we have recently found from a determination of a new class of stacked clusters [18]. Surprisingly, this new structure (shown in Fig. 1) is found to be significantly lower in total energy than the ring structure of Kaxiras and Jackson [12], and 4 eV lower in energy than the dodecahedron. Note that in this structure every atom except for the caps is fourfold coordinated, an important difference from the previously proposed threefold coordinated ring structures [12]. Our Si_{20} (C_{3v}) cluster can be further relaxed to lower symmetry, but the gain in total energy is less than 0.2 eV.

From our QMC calculations we can clearly understand the importance of the different contributions to the total energy, and it is interesting to observe the impact of correlation energies in these clusters, shown in Fig. 2. In particular, for Si_{13} the structure with higher correlation energy is not the most stable, while the opposite is true in the case of Si_{20} where the correlation in the C_{3v} structure is enough to overcome the unfavorable HF energy when compared with the I_h structure. In fact, the correlation energy of the Si_{20} cluster is close to that of the silicon crystal [29]. From this point of view it is remarkable that LDA predicts a correct energy ordering for different competing structures.

The high accuracy of the QMC method and small statistical errors which we were able to achieve opened possibilities to study even more subtle effects such as electron affinity. Thus, we evaluated the electron affinity for the closed-shell Si_{13} cluster with C_{3v} symmetry and found a result of 2.0(1) eV in DMC. Although LDA binds the additional electron self-consistently and predicted the value of the electron affinity rather well with no overbinding (see Table I), it could not determine the correct electronic state of the negative ion cluster. Our QMC results show that by an energy margin of 0.4(1) eV, the additional electron prefers to go into the

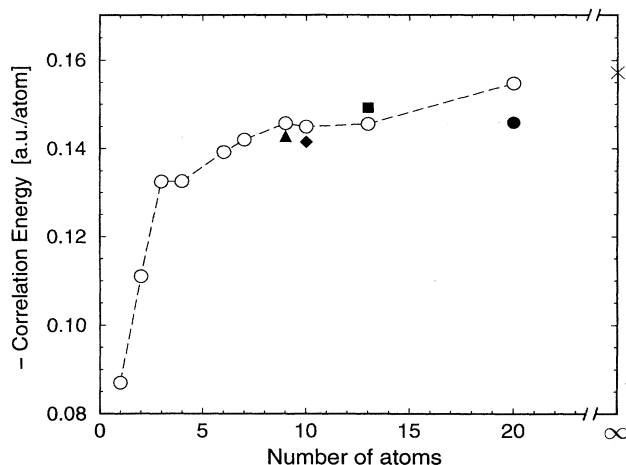


FIG. 2. The (negative) valence correlation energy as a function of the number of atoms in the cluster. The dashed line connects the values which belong to the lowest energy structures. The triangle, diamond, square, and filled circle represent values for Si_9 (C_s), Si_{10} (T_d), Si_{13} (I_h), and Si_{20} (I_h), respectively. The cross at infinite number of atoms corresponds to the estimated correlation energy for the silicon crystal.

singly degenerate A orbital as opposed to the doubly degenerate E orbital predicted by LDA.

Finally, we investigated the possible origin of the few percent discrepancy between experimental and DMC results. There are three possible sources of errors in our DMC calculations: pseudopotential inaccuracies, fixed-node error, and approximate treatment of the nonlocal term in the DMC method. We believe that the main source is the fixed node, and thus we have tried two possibilities to improve the fermion nodes of $\psi_T(R)$. First, for Si_2 we carried out VMC and DMC simulations with a sequence of multiconfiguration trial functions which included up to ~ 20 configurations generated by the multiconfigurational Hartree-Fock (MCHF) [30] method. However, there was no significant near-degeneracy effect and we found practically *no gain* in energy for both VMC and DMC when using these trial functions. Second, we employed a one-configuration trial function but replaced the Hartree-Fock orbitals by natural orbitals which take into consideration the correlation effects. The natural orbitals diagonalize the one-body density matrix [30] and were found by MCHF calculations with single and double excitations into the lowest six virtual orbitals. This trial function gave *lower* VMC and DMC energies, and the difference with experiment decreased by a factor of ~ 2 (see Table II). In order to further test this technique, we applied the same procedure to Si_3 and Si_4 , and a similar improvement in energy was observed. The use of natural orbitals can be considered as an alternative to the approach of Umrigar, Nightingale, and Runge [31], where both the correlation factor and one-body orbitals were optimized within the VMC method for Be and Ne atoms. These results also support the idea of the importance of

TABLE II. Comparison of binding energies (eV/atom) calculated using Hartree-Fock (HF) and natural (NO) orbitals for small clusters.

	DMC (HF)	DMC (NO)	Expt.
Si ₂	1.580(7)	1.592(6)	1.61(4)
Si ₃	2.374(8)	2.423(7)	2.45(6)
Si ₄	2.86(2)	2.92(2)	3.01(6)

using one-body orbitals which are optimal in the presence of correlation [31,32]. Moreover, this raises a new challenge for QMC, namely the task of efficient optimization of one-body orbitals for large systems.

In conclusion, we have carried out QMC calculations of silicon clusters and evaluated valence correlation and binding energies, as well as the electron affinity for one case. Our calculations give an unambiguous picture of the correlation energy in silicon clusters and its role on the energetical ordering of structures. The QMC binding energies agree with available experimental data within a few percent and provide a significant improvement over the mean-field results. For Si₂₀, we discovered a new elongated structure cluster that is energetically more favorable than the previously studied ones by ≈ 2 eV. In addition, for small clusters we have shown that the use of natural orbitals from correlated calculations instead of Hartree-Fock ones gives a trial function which significantly decreases the fixed-node error. We believe that these calculations demonstrate the feasibility and accuracy of QMC for molecular systems with up to about 100 valence electrons and open new perspectives for studying even larger systems in the near future.

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