PHYSICAL REVIEW B VOLUME 50, NUMBER 8 15 AUGUST 1994-II

Improved nonorthogonal tight-binding Hamiltonian for molecular-dynamics simulations of silicon clusters

Pablo Ordejón
Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801

Dmitry Lebedenko
Department of Physics, University of Illinois, Urbana, Illinois 61801

Madhu Menon
Department of Physics and Astronomy, University of Kentucky, Lexington, Kentucky 40506-0055

(Received 10 March 1994; revised manuscript received 5 May 1994)

We present an improvement over the nonorthogonal tight-binding molecular-dynamics scheme recently proposed by Menon and Subbaswamy [Phys. Rev. B **47**, 12 754 (1993)]. The proper treatment of the nonorthogonality and its effect on the Hamiltonian matrix elements has been found to obviate the need for a bond-counting term, leaving only two adjustable parameters in the formalism. With the improved parametrization we obtain values of the energies and bonding distances which are in better agreement with the available *ab initio* results for clusters of size up to $N = 10$. Additionally, we have identified a lowest energy structure for the Si_9 cluster, which to our knowledge has not been considered to date. We show that this structure (a distorted tricapped trigonal prism with C_{2v} symmetry) is also a minimum at the Hartree-Fock level and in approximate density-functional theory, and should therefore be seriously considered as a candidate for the ground-state structure of the Si_9 cluster.

I. INTRODUCTION

The study of small semiconductor clusters has been a very active field of research in the past two decades. From the theoretical point of view, these systems require a fully quantum-mechanical description, due to the strongly directional character of the covalent bond. On the other hand, accurate, full first-principles calculations such as Hartree-Fock with correlation corrections,[1,2] and the local density approximation[3] (LDA) are extremely demanding from the computational point of view. In this context, a number of authors[3–6] have derived approximate, semiempirical tight-binding schemes for the calculation of total energies in silicon clusters. The advantage of the semiempirical tight-binding Hamiltonians is that the system is still described in a quantum-mechanical manner, while the computational effort is kept small, since a minimal (*sp*) atomiclike basis is used and the interaction matrix elements can be parametrized.

Until recently, most of the tight-binding parametrization schemes proposed for the study of silicon clusters have assumed an orthogonal basis of atomiclike states. This basis is not explicitly known and depends on the local environment. This is so because it originates, in principle, from an orthogonalization of the realistic atomic basis, a process that depends on the short and intermediate environment. The Hamiltonian matrix elements obtained using this orthonormal basis are, therefore, not readily transferable from one environment to another. This is especially important in the study of clusters, where a great variety of bonding coordinations and configurations can occur. But even for perfectly tetrahedral bonding, the use of a nonorthonormal basis can have important advantages, as shown by Vergés and Yndurain.[7]

Mercer and Chou[6] have recently proposed to incorporate the effects of the local environment in an orthogonal parametrization by including two-center intra-atomic matrix elements, which depend on the local structure. Alternatively, in order to circumvent the shortcomings of the orthogonal formulations, several authors have developed total energy schemes in terms of nonorthogonal tight-binding formalisms. Sankey and Niklewski[8] developed an approximate first-principles method based on the Harris functional[9] version of LDA. The method was succesfully applied to a variety of systems, including small Si clusters.[10] Menon and Subbaswamy[11] recently proposed a parametrized nonorthogonal tight-binding scheme for the study of silicon clusters (referred to, in this work, as the MS model). The main idea is to obtain a transferable parametrization scheme by including explicitly the effects of the nonorthogonality of the atomic basis. These authors have demonstrated that the inclusion of the nonorthogonality in the tight-binding parametrization leads to a better transferability, reflected particularly in much better vibrational frequencies, while keeping the number of adjustable parameters to a minimum. The same method was applied successfully in the study of carbon clusters and fullerenes.[12,13] In this work, we propose a modification of the MS model, which will allow us to obtain improved results for the minimum energy structures (bonding distances and total energies) of small silicon clusters, while keeping the same number of adjustable parameters. More importantly, we show

0163-1829/94/50(8)/5645(6)/$06.00

that it is possible to obtain improved results even without using any bond-counting term, found necessary in other works.[3,4,11] Our model describes properly the dependence of energy on the local environment by means of the quantum-mechanical electronic energy, so that no further corrections are necessary.

This paper is organized as follows. In Sec. II, we briefly review the main ingredients of the MS model. In Sec. III, we describe the improvements we propose, and the alternative parametrization scheme. In Sec. IV, we present the results of our work, and compare them with earlier *ab initio* studies.[1,2] Finally, we present our conclusions in Sec. V.

II. BACKGROUND: THE MENON-SUBBASWAMY MODEL

In their original work,[11] Menon and Subbaswamy introduced a nonorthogonal tight-binding molecular-dynamics scheme for silicon clusters. Although the details of this method are described in Ref. 11, we will briefly review the main ingredients here. The total energy of the system is described as the sum of three terms:

$$U = U_{\rm el} + U_{\rm rep} + U_{\rm bond}, \tag{1}$$

where $U_{\rm el}$ is the electronic band structure energy, defined as the sum of the one-electron energies ε_k for the occupied states

$$U_{\rm el} = \sum_k^{\rm occ} \varepsilon_k. \tag{2}$$

This term describes the quantum-mechanical bonding energy, and is obtained by diagonalizing the electronic structure Hamiltonian. The particular way in which the Hamiltonian is constructed for a given atomic configuration constitutes the main body of the MS method, and will be discussed in detail later below. $U_{\rm rep}$ is a classical repulsive term that depends on the distances between pairs of atoms

$$U_{\rm rep} = \sum_i \sum_{j>i} \chi(r_{ij}). \tag{3}$$

Menon and Subbaswamy take $\chi(r)$ to be short ranged and to scale exponentially with distance

$$\chi(r) = \chi_0 e^{-\beta(r-d_0)}, \tag{4}$$

where $\beta = 4/r_0$, ($r_0 = 1.12$ Å, one-half of the dimer bond length), and $d_0 = 2.35$ Å (the bond length for the crystal). Finally, following previous works,[3,4] Menon and Subbaswamy introduce an *ad hoc* bond-counting term $U_{\rm bond}$ of the form

$$U_{\rm bond} = -N\left[a(n_b/N) + b\right], \tag{5}$$

where

$$n_b = \sum_i \left[\exp\left(\frac{d_i - R_c}{\Delta}\right) + 1\right]^{-1}, \tag{6}$$

with $R_c = 3.5$ Å and $\Delta = 0.1$ Å. a and b are fitting parameters that are determined so as to bring cohesive energies of several clusters in close agreement with the corresponding *ab initio* values. We will discuss the optimum values of a and b in Sec. III. It is worth noting that although previous workers using the orthogonal tight-binding schemes[3,4] needed a quadratic polynomial for the fitting of the bond-counting term, Menon and Subbaswamy[11] found a linear polynomial (Eq. 5) to be adequate.

We will now focus on how to obtain the Hamiltonian and overlap matrix elements in the MS method. A nonorthogonal basis of atomic orbitals $\{\phi_i\}$ is assumed, in which the Hamiltonian and overlap matrix elements must be computed:

$$H_{ij} = \int \phi_i^* \hat{H} \phi_j d^3r, \tag{7}$$

$$S_{ij} = \int \phi_i^* \phi_j d^3r. \tag{8}$$

The one-electron energies ε_k are obtained by solving the generalized eigenvalue equation

$$(\mathbf{H} - \varepsilon_k \mathbf{S})\mathbf{C}^k = \mathbf{0}. \tag{9}$$

The problem obtaining the matrix elements H_{ij} and S_{ij} is solved using a prescription given by van Schilfgaarde and Harrison.[14] The essential idea is to use universal orthogonal tight-binding parameters (Harrison parameters[15]) V_{ij}, corresponding to matrix elements of the Hamiltonian in an unknown orthonormal basis for tetrahedral compounds, and which, therefore, are not directly transferable between different environments. Van Schilfgaarde and Harrison proposed to construct the nonorthogonal matrix elements from V_{ij} using an approximate prescription derived from the tetrahedral case, in the spirit of the extended Hückel theory.[16] In particular, the overlap matrix elements are given by

$$S_{ij} = \frac{2V_{ij}}{K(\epsilon_i + \epsilon_j)}, \tag{10}$$

and the nonorthogonal Hamiltonian matrix elements by

$$H_{ij} = V_{ij}\left[1 + \frac{1}{K} - S_2^2\right], \tag{11}$$

where

$$S_2 = \frac{(S_{ss\sigma} - 2\sqrt{3}S_{sp\sigma} - 3S_{pp\sigma})}{4} \tag{12}$$

is the nonorthogonality between two sp^3 bonding orbitals. The interaction matrix elements, H_{ij} and S_{ij}, thus obtained are more transferable between different environments than the original orthogonal parameters V_{ij}, since the effect of the different overlaps in different environments is explicitly included.

The overlap and Hamiltonian matrix elements S_{ij} and H_{ij} depend explicitly on the distance between the atoms through the dependence of the universal parameters V_{ij}. These are two-center interactions, which are calculated within the Slater-Koster scheme,[17] as a function of the interatomic distance and the direction cosines of the bond angles. The scaling of the Slater-Koster parameters $V_{\lambda\lambda'\mu}$ is taken to be exponential with the distance d between the two atoms

$$V_{\lambda\lambda'\mu}(d) = V_{\lambda\lambda'\mu}(d_0)e^{-\alpha(d-d_0)}, \qquad (13)$$

where $\alpha = 1/r_0$. This exponent α is taken to reproduce the slope of the Harrison's d^{-2} scaling law[15] for distances close to the equilibrium distance of Si in the bulk diamond structure. This simple exponential scaling is found to be adequate for the clusters we have studied in this work. As in the work of Menon and Subbaswamy, we use Harrison's universal parameters in the context of the Slater-Koster scheme for silicon: $\epsilon_s = -13.55$ eV, $\epsilon_p = -6.52$ eV, $V_{ss\sigma} = -2.37$ eV, $V_{sp\sigma} = 2.52$ eV, $V_{pp\sigma} = 3.32$ eV, and $V_{pp\pi} = -1.07$ eV.

III. THE NEW PARAMETRIZATION SCHEME

We now describe the proposed improvement over the method used by Menon and Subbaswamy, sketched in the preceding section. It is clear from Eq. (10) that the overlap matrix elements S_{ij} must have the same scaling with distance as the Harrison's parameters V_{ij}, since they are proportional. However, the Hamiltonian matrix elements H_{ij} themselves will have a different, more complex scaling, since they also depend on the nonorthogonality parameter S_2, which in turn depends on the overlaps through Eq. (12). Menon and Subbaswamy neglect the effect of distance dependence of S_2, evaluating it at the crystal bond length (d_0), and assume the distance dependence of H_{ij} to arise solely from V_{ij} in Eq. (12). This dependence of S_2 on the distance, however, can have important effects, especially in clusters where the bond lengths are significantly different from those in the bulk crystal. Therefore, the correct treatment of the nonorthogonality for any arbitrary bonding environment requires S_2 to be computed at the actual atomic separation, so that there be no compromising of accuracy and transferability of the Hamiltonian matrix elements. With this in mind, we incorporate the distance dependence of S_2 explicitly in the formalism. As will be shown in Sec. IV this will improve the results significantly, both for the energies and the equilibrium distances of the clusters considered.

Since the details of the scaling of the Hamiltonian matrix elements are different from the work of Menon and Subbaswamy, we had to reoptimize the electronic interaction parameters and the repulsive energy. The scaling exponents of the repulsive energy (β) and the interactions (α) are unchanged. The interaction parameters $V_{\lambda\lambda'\mu}$ which are derived from Harrison's universal scheme, also remain unchanged and not used in the optimization. Thus, the only two adjustable parameters available for fitting in $U_{\rm el}$ and $U_{\rm rep}$ are the overlap parameter K [see Eqs. (10) and (11)] and the coefficient of the repulsive term χ_0 [see Eq. (4)]. We follow the same procedure as in Ref. 11. We determine K and χ_0 by imposing the condition that both the correct bond length (2.24 Å) and the vibrational frequency (511 cm^{-1}) for the Si$_2$ dimer be reproduced. The first condition is fulfilled for every K if χ_0 is given by

$$\chi_0(K) = -0.398K^2 + 2.428K - 2.693, \qquad (14)$$

where χ_0 is in eV. Imposing the second condition fixes the value of K at 1.903, which in turn leads to χ_0=0.486 eV.

We next discuss the bond-counting term given by Eq. (5). As described earlier, this term was introduced *a posteriori* as a correction to the cohesive energies of clusters of different sizes in order to obtain good agreement with the *ab initio* values. Although several authors[3,4,11] have made use of this bond-counting correction to the cohesive energy, its physical origin seems somewhat unclear, if not unjustified. Moreover, its usage in molecular dynamics is particularly awkward, since the magnitude of the correction depends on the number of neighbors of each atom, defined by a somewhat arbitrary cutoff [for example, in Eqs. (5) and (6) the range of the term is given by R_c]. In an *a priori* sense, all the effects of local coordination should already be present in the electronic energy term in Eq. (2). Menon and Subbaswamy found the optimum values for the parameters entering in the bond-counting term [see Eq. (5)] to be $a = 0.75$ eV and $b = -0.25$ eV in their scheme. The relatively large value of a indicates that, in the MS model, the correction to the cohesive energy is largely dependent on the local coordination. Ideally, one would like a to be small, since that would indicate that the electronic energy is accurate enough to describe all the bonding effects. Note that b is an additive constant that only shifts the cohesive energy by the same amount for all systems.

In order to determine the values of a and b in our parametrization scheme, we follow the same procedure as outlined in Ref. 11. We calculate the minimum energy structures of silicon clusters of size up to ten atoms, optimizing the interatomic distances to minimize the energy (the results of this study will be analyzed in Sec. IV). We next determine the optimum values of a and b that will bring the cohesive energies of all the clusters in close agreement with the *ab initio* values.[1,2] We find that the best fit is obtained with $a = 0.08$ eV and $b = -1.4$ eV. We see that these values are quite different from those of Menon and Subbaswamy. In particular, a is very small, suggesting that the correction to the cohesive energy does not significantly depend on the local coordination, and its main effect lies in merely shifting the zero of energy of the atomic states. In fact, we find that very good agreement can also be obtained using $a = 0$ eV and $b = -1.4$ eV. In Table I, we show our results for energies using both sets of parameters, and compare them with the corresponding *ab initio* values,[1,2] and the values obtained by Menon and Subbaswamy.[11]

As can be seen, there is excellent agreement between

TABLE I. Cohesive energies (in eV/atom) for Si$_N$ clusters. Values under Set 1 correspond to our results with $a = 0.08$ eV and $b = -1.4$ eV. Values under Set 2 correspond to our results with $a = 0$ eV and $b = -1.4$ eV. MS correspond to the results of Menon and Subbaswamy.

N	*Ab initio*[a]	Set 1	Set 2	MS[b]
2	1.56	1.49	1.65	1.8
3	2.54	2.53	2.66	2.63
4	3.17	3.23	3.33	3.08
5	3.3	3.4	3.43	3.43
6	3.6	3.61	3.63	3.74
7	3.8	3.73	3.75	3.85
8	3.65	3.67	3.67	3.62
9	3.6	3.61	3.63	3.55
10	3.82	3.78	3.78	3.87

[a] References 1, 2.

[b] Reference 11.

our calculated cohesive energies and the *ab initio* results for all the clusters. We obtain overall improvement over the results of Menon and Subbaswamy, the maximum error being only 0.1 eV for the case $a = 0.08$ eV, and 0.13 eV for $a = 0$ eV, compared to 0.24 eV for MS. The rms deviation is 0.06 eV for $a = 0.08$ eV and 0.09 eV for $a = 0$ eV, compared with 0.12 eV for MS. We stress that improved results are obtained even without the bond-counting term ($a = 0$ case).

IV. RESULTS AND DISCUSSION

In this section, we present the results for Si$_N$ clusters obtained in our study. We will discuss the minimum energy structure for each cluster, as well as the energy difference with other low energy configurations, comparing our results with the *ab initio* values.[1,2] In order to find the minimum energy structures we perform molecular-dynamics simulations for all the clusters. We start with several different sets of random atomic positions and use a simple quenching method, setting the atomic velocities to zero whenever the temperature reaches a maximum. In this way we can also obtain metastable structures. In all cases, we are able to recover the minimum energy structure by annealing and quenching the cluster. In some cases, and in order to compare our results with the *ab initio* values for metastable clusters of certain symmetry, we start with atomic coordinates with the appropriate symmetry. The results for the geometries of the lowest energy structures from $N = 3$ to $N = 10$ are summarized in Table II. The meaning of each of the entries will be explained in the following discussion.

For Si$_3$ we find that the minimum energy structure is an open triangle with C_{2v} symmetry, in agreement with the *ab initio* results.[1] We obtain accurate values for both the bond distance (Si-Si entry) and the bond angle (θ), as shown in Table II. We have also calculated the vibrational frequencies of the cluster and obtain the following values (in cm^{-1}): 130 (a_1 mode), 427 (b_2 mode), and 531 (a_1 mode), compared to the *ab initio* values[1] of 206 (a_1), 560 (b_2), and 582 (a_1). Whereas the frequencies are clearly underestimated in our calculation, the agreement is acceptable, specially if we notice that the orthogonal tight-binding theory[11] gives frequencies about a factor of 2 larger than the *ab initio* results. Moreover, our results show the correct ordering of mode symmetries (a_1, b_1, a_1) whereas in the nonorthogonal model of Menon and Subbaswamy the order is incorrect (a_1, a_1, b_1), although their values are slightly more accurate.

For the Si$_4$ cluster, the minimum energy structure cor-

TABLE II. Optimized molecular geometries (Å) for the Si$_N$ clusters from $N = 3$ to $N = 10$.

Cluster	Structure[a]	Geometrical parameter	*Ab initio*	Present work
Si$_3$	(C_{2v})	Si-Si	2.179	2.239
		θ	77.2°	77.4°
Si$_4$	1[b], (D_{2h})	Si$_1$-Si$_2$	2.303	2.336
		Si$_1$-Si$_3$	2.401	2.516
Si$_5$	8[b], (D_{3h})	Si$_1$-Si$_4$	2.338	2.356
		Si$_1$-Si$_2$	3.256	3.253
		Si$_4$-Si$_5$	2.782	2.845
Si$_6$	16[b], (C_{2v})	Si$_1$-Si$_2$	2.323	2.370
		Si$_2$-Si$_3$	2.651	2.868
		Si$_2$-Si$_4$	2.435	2.506
		Si$_2$-Si$_5$	2.442	2.432
		Si$_4$-Si$_5$	2.364	2.473
Si$_7$	7a[c], (D_{5h})	Si$_1$-Si$_3$	2.472	2.527
		Si$_3$-Si$_4$	2.478	2.474
		Si$_1$-Si$_2$	2.582	2.799
Si$_8$	8b[c], (C_{2h})	Si$_1$-Si$_2$	2.523	2.602
		Si$_2$-Si$_3$	3.144	3.995
		Si$_1$-Si$_5$	2.479	2.548
		Si$_2$-Si$_5$	2.431	2.477
		Si$_1$-Si$_7$	2.231	2.410
		Si$_2$-Si$_7$	2.529	2.523
Si$_9$	Fig. 1, (C_{2v})	Si$_1$-Si$_3$	2.689	2.726
		Si$_1$-Si$_4$	2.557	2.526
		Si$_2$-Si$_3$	2.416	2.439
		Si$_3$-Si$_9$	2.329	2.310
		Si$_4$-Si$_7$	2.742	2.708
Si$_{10}$	10c[c], (C_{3v})	Si$_1$-Si$_2$	2.751	2.907
		Si$_1$-Si$_4$	2.552	2.606
		Si$_4$-Si$_5$	2.540	2.562
		Si$_1$-Si$_7$	2.352	2.430
		Si$_1$-Si$_8$	2.445	2.489
		Si$_4$-Si$_8$	2.543	2.550

[a] The entry under "Structure" correspond to the figures of Refs. 1 and 2 (except for Si$_9$, which corresponds to Fig. 1 of the present work), and the point group of the structure (in parentheses).

[b] Reference 1.

[c] Reference 2.

responds to a planar rhombus (symmetry D_{2h}). This result is in agreement with the *ab initio* calculations,[1] with very similar values of the bond distances (see Table II).

In the case of the Si_5 cluster, the minimum energy structure is found to be a compressed trigonal bipyramid with D_{3h} symmetry (see Fig. 8 of Ref. 1), again in agreement with the *ab initio* results.[2] The bond distances obtained with our method are excellent, as shown in Table II. We have also calculated the difference in energy with other low energy structures considered in Refs. 1 and 2. In particular, for the face-capped tetrahedron (C_{2v}) considered in Ref. 2, we obtain an energy difference with the D_{3h} bipyramid of 0.628 eV, compared with 0.608 eV from the *ab initio* calculations. The square pyramid (Fig. 9 in Ref. 1), with C_{4v} symmetry, is found to have an energy 0.53 eV higher than the D_{3h} bipyramid, again in excellent agreement with the *ab initio* value of 0.45 eV.

For the Si_6 cluster, the *ab initio* calculations[1] predict two lowest energy C_{2v} structures to be nearly isoenergetic. These are a face-capped trigonal bipyramid and an edge-capped trigonal bipyramid (Figs. 15 and 16 of Ref. 1), the energy difference between them being only 0.04 eV. We also find a very small energy difference between these two structures (0.006 eV), with the face-capped being the most stable (whereas in the *ab initio* results the edge capped is lower in energy). We, therefore, conclude that our calculation describes properly the energies of this cluster, since such small difference is clearly beyond our accuracy limits. In Table II we compare our results for the optimized geometry parameters for the edge-capped structure with the *ab initio* values. The agreement is again excellent.

For Si_7 we find that the pentagonal bipyramid (Fig. 7a in Ref. 2) with D_{5h} symmetry is the lowest energy structure, and the tricapped tetrahedron with C_{3v} symmetry (Fig. 7b in Ref. 2) is 0.993 eV higher in energy. There results agree with the *ab initio* calculations, which give an energy difference of 0.952 eV between the two structures. In Table II, we show the bond distances for the minimum energy structure. We also find that a face-capped octahedron (C_{3v}) and a edge-capped octahedron (C_{2v}, see Figs. 7c and 7d in Ref. 2) are stable structures, their energies being 0.739 and 0.823 eV above the pentagonal bipyramid, respectively. The *ab initio* energies for these structures are about 2 eV higher than for the pentagonal bipyramid.

In the case of the Si_8 cluster, the energy minimum corresponds to a distorted bicapped octahedron with C_{2h} symmetry (see Fig. 8b of Ref. 2), 0.554 eV lower than the undistorted D_{3h} bicapped octahedron (Fig. 8a of Ref. 2). Our results agree with the *ab initio* calculations, which predicted an energy difference of 0.56 eV between the two structures. In Table II, we compare our bonding distances with the *ab initio* corresponding values.

The case of Si_9 deserves some discussion. Raghavachari and Rohlfing[2] performed *ab initio* calculations on three possible structures of Si_9: the tricapped octahedron with C_{3v} symmetry, a distorted form of the former, with C_s symmetry, and the tricapped trigonal prism, with D_{3h} symmetry (see Figs. 9a–9c in Ref. 2). At the Hartree-Fock level, the most stable of these structures is a triplet state of the undistorted tricapped octahedron, followed by a singlet state of the distorted tricapped octahedron (0.60 eV higher), and by a triplet state for the tricapped trigonal prism (0.84 eV higher). Inclusion of correlation effects make all the three structures to be almost isoenergetic, with a difference of only 0.1 eV between them. The results of our simulations suggest that the lowest energy structure of Si_9 is none of the above, but rather a distorted form of the tricapped trigonal prism with C_{2v} symmetry (see Fig. 1), with an energy 0.9 eV lower than the other structures. The origin of this structure is a Jahn-Teller distortion of the singlet state of the D_{3h} tricapped trigonal prism. Since this structure was not considered in the *ab initio* works, we have performed an unrestricted Hartree-Fock calculation of the energy of the singlet state of our structure, using the same 6-31G* basis[18] as Raghavachari and Rohlfing. We have optimized the bonding distances to minimize the energy. The result is that, at the Hartree-Fock level, the C_{2v} distorted form of the tricapped trigonal prism is a stable structure for Si_9, with an energy lower than the other structures, except for the C_{3v} tricapped octahedron which is only 0.4 eV lower. Since, as we have mentioned, the correlation effects are important in this cluster, we are unable to decide if our new structure is the ground state of Si_9 at the correlated level, but it is clear that it should be considered as a candidate. To further clarify this issue, we have performed an approximate LDA calculation using the non-self-consistent Harris functional.[9] As we mentioned in the Introduction, this formulation has proven accurate in the description of silicon systems.[8,10] At this level of the theory, the undistorted C_{3v} and D_{3h} structures are metalic, and are, therefore, higher in energy than the distorted clusters. We have relaxed the distorted structures using the approximate LDA forces. The agreement with our predictions is embarrassing with an energy difference of 0.94 eV between the distorted C_s tricapped octahedron and the distorted C_{2v} tricapped trigonal prism, the latter being the most stable. We conclude that the C_{2v} structure is most likely the ground-state structure for the Si_9 cluster.

For Si_{10}, the calculated minimum energy structure (a

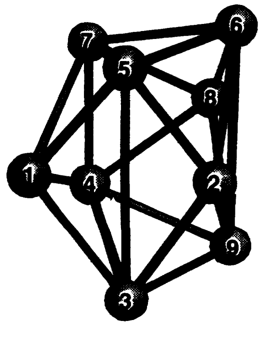

FIG. 1. Minimum energy structure (distorted tricapped trigonal prism with C_{2v} symmetry) of the Si_9 cluster.

tetracapped trigonal prism with C_{3v} symmetry, Fig. 10c in Ref. 2) is 0.67 eV more stable than the T_d tetracapped octahedron (Fig. 10a of Ref. 2). These results agree with the *ab initio* calculation, which shows the same minimum energy structure and an energy difference of 1.04 eV. The bond distances are also in good agreement, as shown in Table II.

We have also considered the Si_{13} cluster, which has recently received considerable attention,[19,20] mainly due to the fact that it is very stable against chemical reactions. Empirical potential calculations suggest that the most stable structure for this cluster is the icosahedron. The LDA calculations,[19] however, find the ground state to be a capped trigonal antiprism with C_{3v} symmetry, with an energy 5.3 eV lower than the icosahedral structure. Quantum-mechanical effects are, therefore, essential in properly describing this cluster. We have performed a calculation of the energy of each of these structures of Si_{13}, relaxing the bond distances (preserving the appropriate symmetry) to obtain the minimum energy. We find that the capped trigonal antiprism is about 2.2 eV lower in energy, in reasonable agreement with the LDA results.

A detailed study of the performance of the present formulation for bulk silicon is presently underway. The main difficulty in extending the application to solid phases is the absence of any cutoff in the interactions with the distance.[11] This is appropriate for clusters, since the number of atoms is finite, but clearly it is not desirable for the bulk material. With the present parameters, the results for silicon in the diamond structure converge only when the cutoff imposed is larger than 9 Å, which indicates that the interactions in the present parametrization are quite long ranged. We obtain a first neighbor distance of 2.45 Å, in reasonably close agreement with the experimental value of 2.35 Å. For the metalic silicon phases the errors are larger due to the close packed nature of the structure, which indicates that the present parameters should be refined to provide accurate results when a cutoff is imposed, making the interactions decay more rapidly.

V. CONCLUSIONS

We have presented an overall improvement over the total energy tight-binding model proposed by Menon and Subbaswamy[11] for the study of silicon clusters. By taking proper account of the variation of the overlap matrix elements with the interatomic distance, and its effect on the nonorthogonal Hamiltonian matrix elements, we have been able to generate an improved parametrization scheme which produced significantly improved results. The most important feature of our scheme is that we can avoid the necessity of an environment-dependent bond-counting term, which was necessary in former works. All the dependence of the energy on the local atomic configurations is correctly described by the quantum-mechanical electronic band structure.

We have studied the stable configurations of silicon clusters with size up to $N = 10$, and also Si_{13}. In all cases we obtain excellent agreement with earlier *ab initio* calculations, both for the configurations with lowest energy and its energy difference with other structures, as well as for the geometrical parameters defining each structure. In addition, we have identified a lowest energy structure for the Si_9 cluster, as a Jahn-Teller distortion of a structure considered in Ref. 2, and shown that this structure is also a likely candidate at the *ab initio* level.

ACKNOWLEDGMENTS

One of us (P.O.) acknowledges funding from DGICyT (MEC, Spain), and partial support from NSF Grant No. DMR-89-20538. One author (M.M.) acknowledges support in part by U.S. DOE Contract No. DE-FC22-93PC93053, and by NSF Grant No. EHR 91-08764. D.L. acknowledges support from NSF Grant No. DMR-91-17822. We also gratefully acknowledge helpful discussions with Dr. K. R. Subbaswamy.

---

[1] K. Raghavachari, J. Chem. Phys. **84**, 5672 (1986).

[2] K. Raghavachari and C. M. Rohlfing, J. Chem. Phys. **89**, 2219 (1988).

[3] D. Tomańek and M. A. Schluter, Phys. Rev. B **36**, 1208 (1987).

[4] K. Laasonen and R. M. Nieminen, J. Phys. C **2**, 1509 (1990).

[5] L. Goodwin, A. J. Skinner, and D. G. Pettifor, Europhys. Lett. **9**, 701 (1989).

[6] J. L. Mercer and M. Y. Chou, Phys. Rev. B **49**, 8506 (1994).

[7] J. A. Vergés and F. Yndurain, Phys. Rev. B **37**, 4333 (1988).

[8] O. F. Sankey and D. J. Niklewski, Phys. Rev. B **40**, 3979 (1989).

[9] J. Harris, Phys. Rev. B **31**, 1770 (1985).

[10] O. F. Sankey, D. J. Niklewski, D. A. Drabold, and J. D. Dow, Phys. Rev. B **41**, 12 750 (1990).

[11] M. Menon and K. R. Subbaswamy, Phys. Rev. B **47**, 12 754 (1993).

[12] M. Menon and K. R. Subbaswamy, Phys. Rev. Lett. **67**, 3487 (1991).

[13] M. Menon, K. R. Subbaswamy, and M. Sawtarie, Phys. Rev. **B 48**, 8398 (1993).

[14] M. van Schilfgaarde and W. A. Harrison, Phys. Rev. B **33**, 2653 (1986).

[15] W. A. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, San Francisco, 1980), and references therein.

[16] R. Hoffmann, J. Chem. Phys. **39**, 1397 (1963).

[17] J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954).

[18] M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees, and J. A. Pople, J. Chem. Phys. **77**, 3654 (1982).

[19] U. Röthlisberger, W. Andreoni, and P. Giannozi, J. Chem. Phys. **96**, 1248 (1992).

[20] J. C. Phillips, Phys. Rev. B **47**, 14 132 (1993).

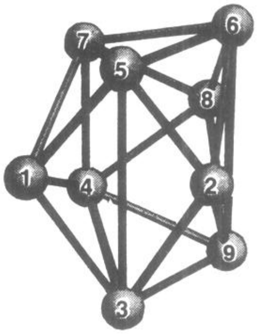

FIG. 1. Minimum energy structure (distorted tricapped trigonal prism with C_{2v} symmetry) of the Si_9 cluster.