Nonorthogonal tight-binding molecular-dynamics study of silicon clusters

Madhu Menon and K. R. Subbaswamy

Department of Physics and Astronomy, University of Kentucky, Lexington, Kentucky 40506-0055
(Received 8 October 1992)

A universal-parameter tight-binding molecular-dynamics technique is detailed and used to obtain equilibrium geometries, energies, and vibrational frequencies of small silicon clusters. With this scheme there is complete agreement with *ab initio* results for the lowest-energy structures of clusters of size up to $N = 10$ (for which *ab initio* results are available). The frequency analysis shows that it is important to include the effects of nonorthogonality in order to obtain reasonable estimates even for small clusters.

I. INTRODUCTION

Since its introduction the tight-binding molecular-dynamics scheme has been found to be very useful in the treatment of covalent systems with tetrahedral coordination.[1] The computational efficiency of the tight-binding method derives from the fact that the Hamiltonian can be parametrized. Harrison's introduction of universal parameters[2] has made this an *a priori* theory in which atoms are characterized only by their valence energies and their covalent radii, all of which are transferable. Tight-binding molecular dynamics incorporating Green's-function methods have been successfully used to determine surface reconstruction, chemisorption sites and bond lengths, defect dynamics, etc. for various semiconductor systems.[3,4]

The conventional molecular-dynamics scheme using the tight-binding theory, while successfully describing covalent systems with tetrahedral coordination, is inadequate when applied to systems dominated by multicenter bonds. For example, it is not possible to obtain the correct vibrational frequency for even a carbon or silicon dimer with this approach. Also, for fullerenes this method yields "breathing mode" and other fundamental frequencies too far removed from experimentally determined values. The problem is due to the fact that while for tetrahedrally coordinated compounds the nonorthogonality between atomic orbitals, responsible for repulsion in the bond, can be separated out as a simple two-body repulsion term (since single two-center bonds dominate the electronic structure), for more general coordination the nonorthogonality cannot be so isolated and it becomes necessary to resort to matrix elements of nonorthogonal atomic orbitals.[5,6] Thus, even the inclusion of next-nearest-neighbor effects requires modifications of the standard formulation. Further, in molecular dynamics the choice of parameters of the tight-binding Hamiltonian depends on the interaction cutoff. While this cutoff can be easily chosen for tetrahedrally coordinated structures, where the bond lengths are clearly defined, no such clear-cut procedure is available for multicoordinated clusters where the bond length fluctuations can be large. Therefore, it is desirable to have a scheme which is insensitive to the chosen cutoff distance, thereby eliminating the complexities associated with arbitrary cutoffs.

With these considerations in mind, we generalize the molecular-dynamics formulation so as to apply for non-tetrahedral and multicoordinated systems. A brief summary of the method has already been published in a shorter article,[7] and we present more details here. Our work is based on a generalization for electronic energy calculations made by van Schilfgaarde and Harrison.[5,6] This allows this universal parameter theory to be applicable (within the usual limits of a one-electron theory) to study the molecular dynamics of molecules, crystals, defects, and surfaces in a computationally tractable way. This particular formulation, while equivalent in spirit to the extended Hückel method popular among chemists,[8] lends itself to first-principles molecular dynamics with significant reduction in computational effort. Explicit incorporation of the nonorthogonality of the basis enables one to treat systems where interactions are dominated by multicenter bonds. This also allows us to model farther neighbor interactions while invoking only one extra parameter, thus preserving the simplicity of the earlier scheme. In this approach the atoms are taken to interact with each other without any cutoff in the interactions between them. This eliminates introduction of spurious forces which could accompany incorrect use of the parameters used for the termination of the interactions.

The present method has already been proven successful in its application to C_{60}.[7] Based on this technique we had predicted that the lowest-energy configuration for an oxygen atom chemisorbed on this molecule is one where the oxygen is bonded over the short bond in C_{60} that is shared by two adjoining hexagons. The underlying double bond is weakened into a single bond in the process. This is termed the "epoxide" structure in chemistry terms, and its formation has now been established experimentally.[9,10] Our estimate of the (A_{1g} symmetry) "breathing mode" and "tangential mode" frequencies for the pristine C_{60} are within 30% of the experimental values. Considering that we are using universal parameters to model the interactions, the agreement is excellent.

In this paper we give details of the present technique both for the evaluation of the forces and binding energies. We then present results for small silicon clusters and compare with other calculations. We stay within the framework of the universal scheme of Harrison[2] for simplicity, making no effort to alter parameters to improve quantitative results.

The past decade has seen a substantial rise in the interest in small and large semiconductor clusters. There have been extensive studies of bulk silicon and its surfaces, both experimentally and theoretically. Experimental investigations of clusters of Si, however, are mainly limited to their mass spectra.[11,12] The theoretical calculations of these clusters fall into three categories: *ab initio*,[13,14] local-density approximation (LDA),[15,16] or semiempirical.[16,17] Another purpose of this paper is to test the validity of our molecular-dynamics scheme by comparing our geometries, binding energies, and frequencies with the above-mentioned work and available experimental results.

II. TECHNIQUE

The highlights of our technique have been published elsewhere.[7] Here we give the details. As in most first-principles molecular-dynamics methods, we solve Newton's equations for atomic motion, with forces computed quantum mechanically (within the Born-Oppenheimer approximation). If the total energy U of a system is known, the force F_x associated with an atomic coordinate x is given by

$$F_x = -\frac{\partial U}{\partial x}. \tag{1}$$

One can then easily do molecular-dynamics simulations by numerically solving Newton's equation

$$m\frac{d^2x}{dt^2} = F_x \tag{2}$$

to obtain x as a function of time. We write U as a sum of three terms,[1,16]

$$U = U_{el} + U_{rep} + U_{bond}, \tag{3}$$

where U_{el} is the sum of the one-electron energies E_k,

$$U_{el} = \sum_{k}^{occ} E_k, \tag{4}$$

and U_{rep} is given by a repulsive pair potenial $\chi(r)$:

$$U_{rep} = \sum_{i}\sum_{j(>i)} \chi(r_{ij}). \tag{5}$$

Here r_{ij} is the separation of atoms i and j. $\chi(r)$ is short ranged and taken to scale exponentially with distance.[4]

$$\chi(r) = \chi_0 e^{-\beta(r-d)}, \tag{6}$$

with $\beta = 4/r_0$, and r_0, a natural unit of distance in our simulations, is taken to be one-half the dimer bond length. d is the sum of covalent radii of interacting atoms.

We find this simple exponential distance dependence adequate for our purposes. The term U_{bond} will be described later below.

We now turn our attention to the evaluation of the electronic part of the force. Let $\{\phi_a\}$ be a set of atomic orbitals centered on different atoms in the cluster. This set is, therefore, nonorthogonal. One can write the variational wave function for the system as

$$\psi_n = \sum_{a} c_a^n \phi_a. \tag{7}$$

The characteristic equation then becomes

$$\sum_{j}(H_{ij} - E_n S_{ij})c_j^n = 0, \tag{8}$$

where

$$H_{ij} = \int \phi_i^* H \phi_j \, d^3r \tag{9}$$

and

$$S_{ij} = \int \phi_i^* \phi_j \, d^3r. \tag{10}$$

In matrix form Eq. (8) becomes

$$(\mathbf{H} - E_n\mathbf{S})\mathbf{C}^n = 0, \tag{11}$$

where $\mathbf{C}^n$ is a column vector. Taking the Hermitian conjugate of (11),

$$\mathbf{C}^{n\dagger}(\mathbf{H} - E_n\mathbf{S}) = 0, \tag{12}$$

where we have used the fact that $\mathbf{H}$ and $\mathbf{S}$ are Hermitian. Differentiating (11) with respect to x, we get

$$\left[\frac{\partial}{\partial x}(\mathbf{H} - E_n\mathbf{S})\right]\mathbf{C}^n + (\mathbf{H} - E_n\mathbf{S})\frac{\partial}{\partial x}\mathbf{C}^n = 0. \tag{13}$$

Multiplying on the left with $\mathbf{C}^{n\dagger}$ and using (12), we have

$$\mathbf{C}^{n\dagger}\left[\frac{\partial}{\partial x}(\mathbf{H} - E_n\mathbf{S})\right]\mathbf{C}^n = 0. \tag{14}$$

From this we get

$$\frac{\partial E_n}{\partial x} = \frac{\mathbf{C}^{n\dagger}(\frac{\partial \mathbf{H}}{\partial x} - E_n\frac{\partial \mathbf{S}}{\partial x})\mathbf{C}^n}{\mathbf{C}^{n\dagger}\mathbf{S}\mathbf{C}^n}. \tag{15}$$

The $\mathbf{C}^n$ are normalized so that

$$\mathbf{C}^{\dagger}\mathbf{S}\mathbf{C} = 1. \tag{16}$$

The traditional approach with nearest-neighbor cutoff is to set $\mathbf{S} = 1$,[1,16,17] and to use Slater-Koster form for the Hamiltonian matrix elements.[18] We call this the orthogonal tight-binding approach. As mentioned above, and discussed in detail by van Shilfgaarde and Harrison,[5] for multicoordinated systems the nonorthogonality cannot be separated out as a two-body repulsion term, and the effect of the nonorthogonality must be dealt with explicitly. The additional complication of calculating the overlap matrix was dealt with by van Schilfgaarde and Harrison[5] in the spirit of extended Hückel theory,[8] where

a proportionality is assumed between **H** and **S**:

$$H_{ij} = \frac{K}{2}(H_{ii} + H_{jj})S_{ij}. \tag{17}$$

While in extended Hückel theory **S** is explicitly calculated assuming Slater-type atomic orbitals, and **H** from the above proportionality, in van Schilfgaarde and Harrison's approach **H** is computed as in orthogonal tight-binding theory, using universal parameters, and **S** is in turn determined from the above proportionality. Specifically, if V_{ij} denote the Hamiltonian matrix elements in orthogonal theory, van Schilfgaarde and Harrison showed that

$$H_{ij} = V_{ij}\left[1 + \frac{1}{K} - S_2^2\right], \tag{18}$$

where

$$S_2 = \frac{(S_{ss\sigma} - 2\sqrt{3}S_{sp\sigma} - 3S_{pp\sigma})}{4} \tag{19}$$

is the nonorthogonality between sp^3 hybrids. The quantities $S_{\lambda\lambda'\mu}$ in turn are determined from

$$S_{\lambda\lambda'\mu} = \frac{2V_{\lambda\lambda'\mu}}{K(\varepsilon_\lambda + \varepsilon_{\lambda'})}. \tag{20}$$

The orthogonal Hamiltonian parameters $V_{\lambda\lambda'\mu}$ are obtained from the dimensionless universal parameters through a prescription given by Harrison[2] and used successfully for tetrahedral compounds. The only additional parameter entering this scheme is the Hückel proportionality constant K, whose determination is discussed in the next section. The complete set of V_{ij}'s necessary for the construction of the Hamiltonian matrix in (18) are obtained in terms of the parameters $V_{\lambda\lambda'\mu}$ and direction cosines (l,m,n) of the bond vector $\vec{d}$ using the standard Slater-Coster scheme.[18] The $V_{\lambda\lambda'\mu}(d)$ are taken to decrease exponentially with d:

$$V_{\lambda\lambda'\mu}(d) = V_{\lambda\lambda'\mu}(d_0)e^{-\alpha(d-d_0)}, \tag{21}$$

where d_0 is the bond length for the crystal and $\alpha = 1/r_0$. This exponential scaling of parameters could easily be modified if deemed necessary (e.g., algebraic dependence in the vicinity of nearest-neighbor distances, but exponential dependence farther out), but we find this simple exponential dependence adequate for our purposes.

The eigenvalues of a system with nonorthogonal basis set, for obtaining the electronic part of the force, can then be obtained from

$$\det|H_{ij} - ES_{ij}| = 0. \tag{22}$$

Evaluation of (22) is expedited by the use of the well-known Cholesky factorization in which S is factored into

$$\mathbf{S} = \mathbf{BB}^T. \tag{23}$$

This factorization is always possible provided S is positive definite. The eigenvalue problem is then equivalent to solving

$$\det|B^{-1}H(B^T)^{-1} - E| = 0, \tag{24}$$

where $B^{-1}H(B^T)^{-1}$ is real symmetric and can be solved by standard methods. Finally, the electronic part of the force is given by[1]

$$F_x^{\text{el}} = \sum_k^{\text{occ}} \frac{\partial E_k}{\partial x}. \tag{25}$$

Note that the traditional orthogonal tight-binding formalism can easily be recovered from the above by setting K to a large value, and keeping only nearest-neighbor interactions.

The first two terms on the right-hand side of (3) are not sufficient to exactly reproduce cohesive energies of dimers through bulk structures. This is because there are several components contributing to the total energy in tight binding theory. They include the promotion energy required to transform from free atom to hybrids necessary to form covalent bonds, and covalent, metallic, polar, and overlap energies.[2] It is possible to include all these components in U_{el} and U_{rep} by a proper choice of parameters for bulk structures. For clusters of arbitrary sizes, however, where coordination of atoms varies considerably, an extra bond-counting term, U_{bond}, is necessary to reproduce cohesive energies accurately as shown by Tomának and Schluter.[16] This term can be chosen to bring binding energies in agreement with the *ab initio* values, as described below.

III. RESULTS AND DISCUSSION

The electronic parameters we use for Si are generated using Harrison's[2] universal parameter scheme, and listed in Table I. Once again we emphasize that to preserve the *a priori* nature of the calculation we have chosen not to use other parametrization schemes known to yield better results for bulk Si, e.g., that of Chadi and Cohen.[19]

The two remaining parameters are the coefficient of the repulsive term χ_0 [see Eq. (6)] and the overlap parameter K [see Eq. (17)]. We impose the condition that the correct (experimental) bond length (2.24 Å) (Ref. 20) for the silicon dimer be reproduced. This makes the two parameters mutually dependent as shown in Fig. 1. As can be seen in the figure, the dependence is very smooth. It can be fitted by the quadratic form

$$\chi_0(K) = -0.45K^2 + 2.10K - 1.42, \tag{26}$$

where χ_0 is in eV. We are still free to choose K, which we fix by the requirement of obtaining the correct (ex-

TABLE I. Silicon parameters derived from universal scheme (Ref. 2).

Parameters	eV
ϵ_s	-13.55
ϵ_p	-6.52
$V_{ss\sigma}$	-2.37
$V_{sp\sigma}$	2.52
$V_{pp\sigma}$	3.32
$V_{pp\pi}$	-1.07
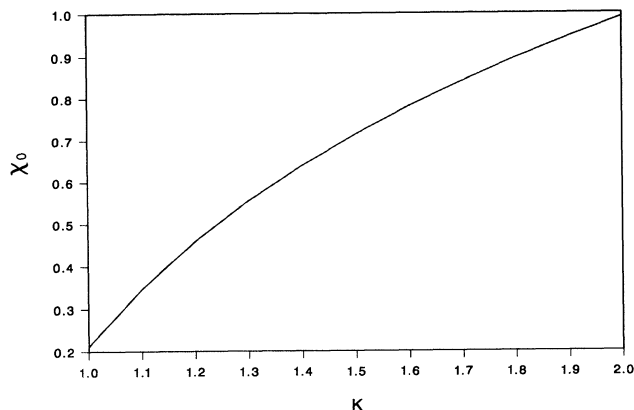
FIG. 1. Dependence of the coefficient of the repulsive term χ_0 on the overlap parameter K.
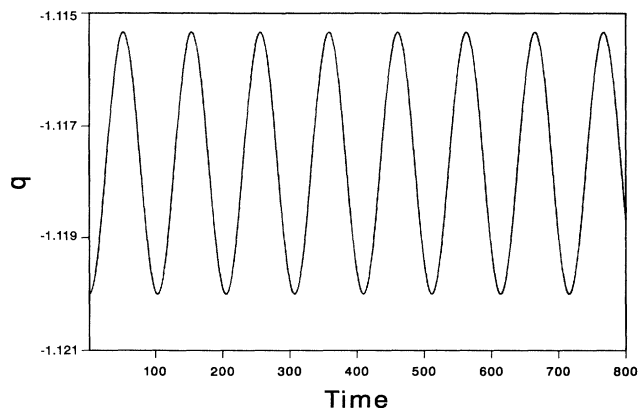

FIG. 2. Simulation run for one of the silicon atoms in a dimer. q is the coordinate along the bond in Å. The unit of time in the simulation is 6.37×10^{-16} s. This time-dependent radial motion gives a vibrational frequency of 511 cm^{-1}.

perimental) vibrational frequency for the dimer (511 cm^{-1}).[20] The value we use is $K = 1.25$, although the results are not very sensitive to the precise value of K in this range. Thus, with the requirement of reproducing the correct bond length and frequency for the dimer we have exhausted all disposable parameters.

In Fig. 2 we show the motion along the bond of one of the silicon atoms in a dimer for one simulation run. The unit of time step for all simulations is 6.37×10^{-16} s. The time-dependent radial motion shown in the figure yields a vibrational frequency of 511 cm^{-1}. This value also agrees with the value obtained from a conventional small oscillation dynamical matrix calculation. Recall that the repulsive parameter χ_0 and the nonorthogonality constant K were set by requiring the dimer bond length and frequency to agree with experimental values. These same values are then used for all clusters.

We have carried out calculations for silicon clusters of size up to ten atoms. We begin the simulation by starting with a configuration which is nearly in the desired form. The atoms are then allowed to relax by removing a small fraction ($\leq 1\%$) of each of the velocity components at every time step.

To determine cohesive energies, we first need to fix the bond-counting term as discussed in the preceding section. Tomanek and Schluter[16] used a quadratic polynomial with a sharp cutoff for counting bonds, while Laasonen and Nieminen[17] used the same quadratic polynomial with a smooth cutoff. We also employ a smooth cutoff, and find that a linear polynomial is adequate in our nonorthogonal scheme:

$$U_{\text{bond}} = -N[a(n_b/N) + b], \qquad (27)$$

where

$$n_b = \sum_i \left[\exp\left(\frac{d_i - R_c}{\Delta} \right) + 1 \right]^{-1}, \qquad (28)$$

where the sum is over all bonds. We take $R_c = 3.5$ Å and $\Delta = 0.1$ Å. This procedure is the same as that of Laasonen and Nieminen.[17] We emphasize that R_c in our work is not a cutoff distance for interaction, but merely a

distance for calibrating the energy term. There is *no* cutoff distance for forces between atoms in our scheme. The values for a and b in Eq. (27) were determined so as to bring our total energies for the entire set of 19 clusters we considered to be in reasonable agreement with the corresponding *ab initio* values.[13,14] The values we choose are $a = 0.75$ eV and $b = -0.25$ eV. In Table II we compare our calculated energies (per atom) for our lowest-energy structure for each N with the corresponding *ab initio* energies.[13,14]

The minimum energy structure we find for $N = 3$ is an open triangle with D_{2h} symmetry. For $N = 4$ we find the stable structure to be a rhombus (D_{2h} symmetry). These results are in agreement with all previous calculations.[13,17,16] For $N = 5$, we find two low-energy structures. Of these, the strongly compressed trigonal bipyramid with apex atoms holding the triangle together, shown in Fig. 3, is found to be lower in energy, in agreement with the *ab initio* results.[13] We also find an energy minimum for a low symmetry structure,[17] although this structure was 0.55 eV higher in energy. This latter structure was not considered by Raghavachari.[13] Laasonen and Nieminen[17] also found a very small energy

TABLE II. Cohesive energies per atom for Si$_N$.

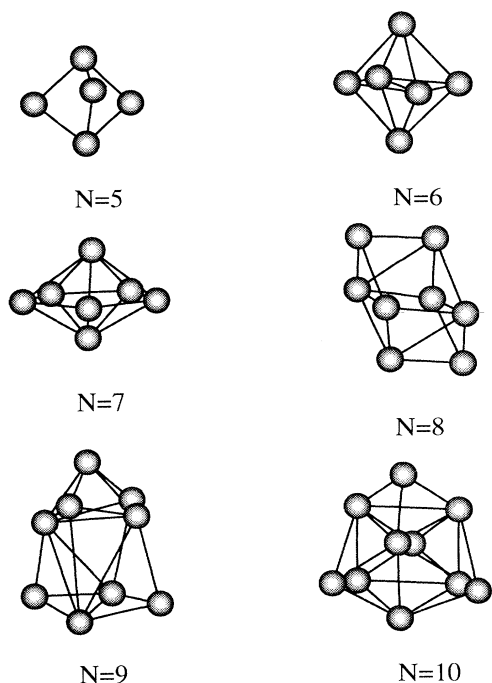| N	E/N (*ab initio*[a]) eV	E/N (present) eV
2	1.56	1.80
3	2.54	2.63
4	3.17	3.08
5	3.3	3.43
6	3.6	3.74
7	3.8	3.85
8	3.65	3.62
9	3.6	3.55
10	3.82	3.87

[a] References 13 and 14.

FIG. 3. Geometries of the lowest-energy structures of small silicon clusters from $N = 5$ to 10 obtained using the present molecular-dynamics scheme.

difference between these two structures, with the latter structure lower in energy for one set of parameters. This orthogonal tight-binding finding is in disagreement with the ab initio results and with our result. In all cases our calculated bond lengths are systematically higher than the ab initio values of Raghavachari[13] by 5–7 %.

In Table III we compare vibrational frequencies for the dimer and the trimer obtained by both orthogonal and nonorthogonal tight-binding molecular-dynamics schemes with ab initio values. The orthogonal theory gives frequencies that are almost a factor of 2 higher than the nonorthogonal theory, with the latter being in good agreement with ab initio values. It is clear from this table that the orthogonal scheme, while reasonably adequate for determining structures and energies for small clusters, cannot be relied on to give reasonable estimates for frequencies, even for smaller clusters. This also appears to be the case for larger clusters as shown by our work on C_{60}.[7]

For $N = 6$, the edge-capped (distorted) trigonal bipyramid (see Fig. 3) has the lowest energy ($E =$

−22.44 eV), although it is only 0.54 eV higher in energy compared with the face-capped trigonal bipyramid. The ab initio method[13] also gives close energies for these two structures with lower energy for the first structure as in our method. By contrast, Laasonen and Nieminen[17] found the latter structure to be slightly lower in energy over the former.

In the case of Si_7, we find the pentagonal bipyramid (Fig. 3) to be the most stable with $E = -26.95$ eV. We also find an energy minimum for a tricapped tetrahedron ($E = -25.34$ eV) as in earlier works. These results agree with earlier results.[14,16,17]

For $N = 8$, the distorted bicapped octahedron was found to be the lowest-energy structure ($E = -28.96$ eV), in agreement with ab initio result.[14] The undistorted bicapped octahedron was also found to be an energy minimum ($E = -27.04$ eV). Another minimum was obtained for the tetracapped tetrahedron ($E = -28.16$ eV), which was the lowest-energy structure found in the orthogonal tight-binding method.[17]

For $N = 9$, we obtained lowest energy ($E = -31.95$ eV) for the distorted tricapped octahedron, once again in agreement with Raghavachari.[14] The tricapped trigonal prism was found to be another energy minimum with $E = -30.78$ eV. In the orthogonal tight-binding method[17] this latter structure was found to be lower in energy over the former by 1.8 eV.

For $N = 10$ we find two low-energy structures. Of these, the tetracapped trigonal prism (Fig. 3) was found to be lower in energy ($E = -38.65$ eV) over the tetracapped octahedron ($E = -35.80$ eV). This is in agreement with the recent ab initio work[21] and density-functional calculations[15] which find the former structure being the ground state with the latter slightly higher in energy. This is also in agreement with the results of Laasonen and Nieminen,[17] who find an energy difference of about 3 eV between these two structures with the former structure being more stable. For the tetracapped octahedron we obtain a side length of 3.4 Å and a cap bond length of 2.6 Å. This is in agreement with the results of Tomǎnek and Schluter[16] who find the bond lengths to be 3.1 and 2.4 Å, respectively, in their tight-binding energy minimization scheme. Their corresponding bond lengths using the LDA energy minimization scheme are 2.5 and 2.3 Å, respectively. The ab initio work,[14] however, seems to indicate a reversal of ordering in the bond lengths with the corresponding bonds being 2.4 and 2.6 Å, respectively.

Another structure considered by earlier works[16,14] for $N = 10$ is the adamantane fragment (i.e., the building block for bulk silicon). We find this structure to

TABLE III. Comparison of frequencies obtained by orthogonal and nonorthogonal tight-binding molecular-dynamics methods with the ab initio method.

N	Orthogonal TB cm^{-1}	Nonorthogonal TB cm^{-1}	ab initio[a] cm^{-1}
2	947	511	507
3	$520(a_1),930(b_2),1026(a_1)$	$234(a_1),525(b_2),493(a_1)$	$206(a_1),560(b_2),582(a_1)$

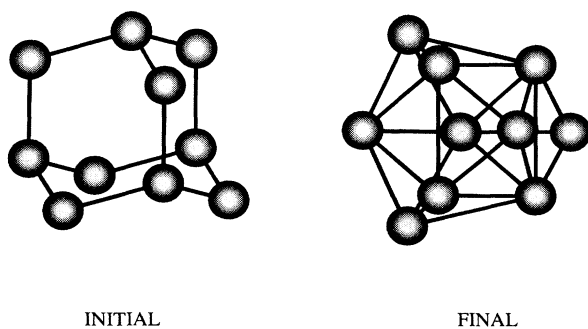[a] Reference 13.

INITIAL   FINAL

FIG. 4. Simulation showing the instability of the adamantane fragment (building block for crystalline silicon). We start with an ideal adamantane structure (initial) and find this structure to be unstable, distorting into a more compact tetracapped trigonal prism (final), our ground-state structure for $N = 10$.

be unstable in our simulations, distorting into a tetracapped trigonal prism, which is our lowest-energy structure. The initial and final stages of this simulation runs are shown in Fig. 4. Both Raghavachari[14] and Tomanek and Schluter[16] found the adamantane structure to be considerably higher in energy than both the tetracapped octahedron and the tetracapped trigonal prism, but did not report on its stability.

We note that the orthogonal tight-binding molecular-dynamics scheme seems to favor a close-packed structure for clusters of size $N = 8$ and 9.[17] Our results, on the other hand, favor octahedron structures over close-packed structures, in agreement with the ab initio work.[14] The larger clusters tend to be multicoordinated with many atoms forming bonds in excess of 4. As explained earlier, the traditional orthogonal tight-binding methods become less reliable when used to treat these systems. The present method, however, treats systems dominated by multicenter bonds more accurately and

hence is more reliable for the treatment of larger clusters with arbitrary coordinations.

IV. CONCLUSION

We have presented the details of a recently developed nonorthogonal tight-binding molecular-dynamics scheme which correctly treats nontetrahedral and multicoordinated structures, and shown its application to silicon clusters. The present scheme maintains the simplicity of the original orthogonal tight-binding theory and, by explicitly treating the nonorthogonality of the basis, greatly extends the applicability of earlier orthogonal schemes to include systems where extended Hückel methods have proven useful. All these have been made possible by the addition of only one extra parameter. The absence of any cutoff in the interactions between atoms in our theory eliminates introduction of undesirable spurious forces that are sometimes present in dynamical schemes.

The frequency analysis shows considerable improvement in the estimates of vibrational frequencies for silicon clusters over the orthogonal tight-binding molecular-dynamics scheme where such estimates tend to give frequencies that differ by a factor of 2 or larger. It is important to include effects of nonorthogonality for obtaining reasonable estimates even for small clusters.

We have shown that the present scheme reproduces lowest-energy structures obtained by ab initio methods for clusters of size up to $N = 10$, in contrast to the orthogonal tight-binding scheme which gives results in disagreement for $N = 5$, 6, 8, and 9. The present scheme can be relied on to give better results for geometries for larger multicoordinated structures than the conventional orthogonal tight-binding scheme.

ACKNOWLEDGMENTS

[1]M. Menon and R. E. Allen , Phys. Rev. B 33, 7099 (1986).

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

[3]R. E. Allen and M. Menon, Phys. Rev. B 33, 5611 (1986).

[4]M. Menon and R. E. Allen, Phys. Rev. B 38, 6196 (1988).

[5]M. van Schilfgaarde and W. A. Harrison, J. Phys. Chem. Solids 46, 1093 (1985).

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

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

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

[9]K. M. Creegan, J. L. Robbins, W. K. Robbins, J. M. Millar, R. D. Sherwood, P. J. Tindall, D. M. Cox, A. B. Smith III, J. P. McCauley, Jr., D. R. Jones, and R. T. Gallagher, J. Am. Chem. Soc. 114, 1103 (1992).

[10]Y. Elemes, S. K. Silverman, C. Sheu, M. Kao, C. S. Foote, M. M. Alvarez, and R. L. Whetten, Angew. Chem. Int. Ed. Engl. 31, 351 (1992).

[11]O. Echt, K. Sattler, and E. Recknagel, Phys. Rev. Lett. 47, 1121 (1981).

[12]L. A. Bloomfield, R. R. Freeman, and W. L. Brown, Phys. Rev. Lett. 54, 2246 (1985).

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

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

[15]P. Ballone, W. Andreoni, R. Car, and M. Parinello, Phys. Rev. Lett. 60, 271 (1988).

[16]D. Tomanek and M. Schluter, Phys. Rev. B 36, 1208 (1987).

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

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

[19]D. J. Chadi and M. L. Cohen, Phys. Status Solidi 68, 405 (1975).

[20]K. P. Huber and G. Herzberg, Constants of Diatomic Molecules (Van Nostrand Reinhold, New York, 1979).

[21]K. Raghavachari and C. M. Rohlfing, J. Chem. Phys. 198, 521 (1992).