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A COMPARISON OF DIFFERENT ORTHOGONAL TIGHT-BINDING MOLECULAR DYNAMICS SIMULATION METHODS FOR SILICON CLUSTERS

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In the present work different orthogonal tight-binding molecular dynamics methods have been employed for describing small silicon clusters. The cohesive energies calculated using these methods have been compared with those found from the first principles Car-Parrinello method. The comparison shows that the orthogonal tight binding matrix elements and repulsive potentials need to include the radial cutoff up to fourth neighbor distance in diamond structure in order to reproduce *ab initio* results. The environmental correction is not needed in this orthogonal tight-binding method.

Keywords: Orthogonal tight binding methods; Silicon clusters

1. INTRODUCTION

At present there exists a fairly good understanding of the properties of single atoms and molecules, as well as those of at least one class of solids namely the crystalline solids. The latter category of matter in the bulk form consists of aggregates of a large number of atoms ($\sim 10^{23}$ atoms per unit volume). It is also well known that solids exhibit many properties like conductivity, elasticity, susceptibility etc. which are simply not present in their elementary constituents namely the atoms. So the question that naturally comes to one's mind is at what aggregates of atoms do the bulk properties arise? The answer to this fundamental question, it is believed, will emerge from the study of atomic clusters. Besides this motivation, production and deposition of atomic clusters on suitable substrates provides another route for the generation of nanomaterials, which are of tremendous technological importance. Silicon is the material of electronic industry. One of the major thrust in this area is miniaturization and with its progress it might reach the small silicon clusters pretty soon. Hence there is a need

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for studying and understanding the electronic properties of Si clusters, which is the present motivation behind this work.

First principles quantum mechanical calculations such as the Car-Parrinello method within the generalized gradient approximation (CP-GGA) is successful in predicting the structures of Si clusters up to twenty atoms (Shvartsburg et al. (2000)). While the CP-GGA method is very accurate in yielding valuable informations about the structure and electronic properties of these clusters, the demand on computational time to optimize medium sized clusters for longer time scales is enormously high. On the other hand the empirical tight binding methods are very popular due to rather low computational time requirements since the potentials in these methods are based on the interparticle separations of the atomic positions without involving the electron coordinates as is the case in the first principles methods. Since these methods require only the atomic positions in a cluster, a large time step can be safely taken in the molecular dynamics simulation. The other computational advantage of this method is that the Hamiltonian can be parameterized containing the effect of angular forces in a natural way by the Slater-Koster method (Slater and Koster, 1954). While the orthogonal tight-binding schemes assume that the orbitals of each atom remain orthogonal at all times, the non-orthogonal schemes treat their overlap explicitly. The disadvantage of the nonorthogonal method is that the overlap matrix makes the calculation slower.

In the orthogonal tight binding methods the potentials for the diamond structure are determined by fitting the parameters so as to reproduce all the physical quantities accurately. The potentials are then made transferable to include the position dependence by introducing some scaling function such that the bulk structural phases, properties of point defects, surfaces and clusters of Si can be computed by molecular dynamics simulations. Generating the accurate transferability of the tight-binding potentials from the bulk diamond structure with tetrahedral bonding to non-tetrahedral and multi-coordinated Si clusters where the major bonding is metallic, is a very challenging task. During past several years, a lot of efforts has been devoted to the development of a suitable transferable tight-binding method to optimize small Si clusters. Since very accurate geometries and cohesive energies of Si clusters up to Si₂₀ have been optimized in the CP-GGA method, it is worth comparing different orthogonal tight-binding methods to find the most efficient one in understanding the small Si clusters.

2. METHOD OF CALCULATIONS

The potentials in the orthogonal tight-binding scheme within the Slater–Koster method are based on the two-center hopping integrals. In the minimal (s, p) representation only four hopping integrals $h_{ss\sigma}$, $h_{sp\sigma}$, $h_{pp\sigma}$ and $h_{pp\pi}$ are necessary to calculate all the matrix elements of the Hamiltonian. The repulsive potential which arises when two atoms are brought together is dependent on the position vector separating the atomic coordinates.

Summarizing all the tight binding methods which study Si clusters containing N atoms, we find the following expression for the binding energy

$$E = \sum_{i=1}^{N} \frac{p_i^2}{2M} + E_{bs} + E_{rep} + C \sum_{i=1}^{N} (q_i - q_i^0)^2.$$
(1)

The first term is the kinetic energy of the atoms with mass M. The second term is the electronic energy obtained from the orthogonal tight-binding methods. The third term E_{rep} represents the repulsive energy. In the fourth term q_i and q_i^0 are the Mulliken charges of the *i*th atom in a cluster and *i*th neutral atom, respectively. This is a Hubbard-like on-site energy term which corrects the charge transfer from one atom to the another in a cluster, thus making it sure that the charge neutrality is preserved while performing molecular dynamics simulations in a cluster. However, this energy term is very small in a neutral cluster. The band energy E_{bs} is given by

$$E_{bs} = 2\sum_{k}^{occ.} f(\epsilon_k, T)\epsilon_k - 2n(\epsilon_s + \epsilon_p),$$
⁽²⁾

where $f(\epsilon_k, T)$ is the Fermi–Dirac distribution function obtained for the single particle energy ϵ_k and temperature T. The single particle energies are obtained by diagonalizing the Hamiltonian real space constructed using the Slater–Koster (1954) method. The second term in Eq. (2) is the energy of n isolated atoms with ϵ_s and ϵ_p being the on-site energies of the s and p electrons, respectively.

The repulsive energy E_{rep} is given by

$$E_{rep} = \sum_{i} \sum_{j \neq i} \Phi(r_{ij}) - E_{bc}, \qquad (3)$$

where $\Phi(r_{ij})$ is the pair repulsive potential, r_{ij} being the distance between the *i*th and *j*th atoms with position vectors \mathbf{r}_i and and \mathbf{r}_j , respectively. E_{bc} is the energy due to the bond correction,

$$E_{bc} = n[c_1(n_b/n)^2 + c_2(n_b/n) + c_3].$$
(4)

Here n_b is the number of bonds and c_1 , c_2 and c_3 are adjustable parameters. Since the number of bonds are different in different clusters, this term represents the environmental correction to the binding energy of a cluster.

The molecular dynamics simulations method is based on the solution of the Newton's equation where the updated positions are calculated as

$$\mathbf{r}_{i}(t+\delta t) = \mathbf{r}_{i}(t) + \mathbf{v}_{i}(t)\,\delta t + 12\mathbf{a}_{i}(t)(\delta t)^{2},\tag{5}$$

where \mathbf{v}_i and \mathbf{a}_i are the velocity and acceleration of the *i*th atom which are calculated from the total force exerted on the atom. The total force is the combination of the attractive electronic force and repulsive force. While the electrostatic repulsive force is calculated directly, the electronic force is calculated using the Hellman–Feynman method. The velocity-Verlet scheme is applied to move atoms in a cluster until the forces are small. The quenching method has been employed to search the minimum energy of a cluster. All tight binding methods are spin-unpolarized.

3. COMPARISON OF DIFFERENT METHODS

In this section a comparative study will be made of several orthogonal tight-binding methods existing in the literature. All the methods studied here are spin-unpolarized.



FIGURE 1 Optimized geometries of Si clusters up to n = 19. For Si₁₉ cluster, both cage-like (19a) and prolate (19b) structures are presented.

The merit of a method is judged by comparing its cohesive energy with those obtained using CP-GGA method. We have taken the optimized geometries of CP-GGA method to calculate cohesive energies. The geometries of Si clusters up to n = 19 are shown in Fig. 1. The cohesive energies obtained from different methods are shown in Fig. 2.

3.1. Harrison Scaling Method

The early attempt by Tománek and Schlüter (1987) to optimize small Si clusters up to fourteen atoms using the empirical orthogonal tight binding scheme is based on the



FIGURE 2 Lowest energy structures of small Si clusters calculated using different orthogonal tight-binding models. The solid, long-dashed, dashed, dotted and dot-dashed lines correspond to methods of CP-GGA, Lenosky *et al.* (1997), IGPS, Sawada and GPS (Goodwin *et al.*, 1989) models, respectively.

Harrison scaling method (Harrison, 1980) where the hopping integrals are represented as

$$h_{\alpha}(r) = h_{\alpha}(r_0) \left(\frac{r_0}{r}\right)^2,\tag{6}$$

 r_0 is the nearest neighbor distance in the diamond lattice structure and the hopping matrix elements in the diamond structure, $h_{\alpha}(r_0)$ are taken from the work of Harrison (1980). Later this method has been used by Rantala *et al.* (1990) to study linear and non-linear properties of small Si clusters. In this method the cohesive energy of the clusters are calculated taking all the terms described in Eqs. (1)–(4). The repulsive potential is obtained as a difference between the *ab initio* binding energy of Si₂ and the corresponding tight-binding energy defined in Eq. (2). In Fig. 2 we have not shown the cohesive energies obtained using this method as they do not compare well with the CP-GGA results. The reason behind the poor reproducibility of the cohesive energies in this method is that the Harrison scaling method makes the potential long-ranged for which the matrix elements are non-negligible at higher order neighbors. As a result of this the method fails to find structural phases of Si. The equilibrium volume of the FCC lattice is overestimated by almost a factor of two. The method gives approximate cohesive energies by including the bond correction energy term where the number of bonds are counted case-by-case basis for each

TABLE I Physical properties of Si₂ clusters in different orthogonal tight-binding models are compared with the experiment. The notations for models are Tománek-Schlüter model (TS) (Tománek and Schlüter, 1987) Kohyama model (Kohyama, 1991), GPS model (Goodwin *et al.*, 1989), Improved GPS model (1994) and cubic spline model (CS) by Lenosky *et al.* (1997). The experimental cohesive energy U_{exp} , bond length ℓ and vibrational frequency ω_v are taken from Huber and Herzberg (1979), respectively

Property	Experiment	TS	Kohyama	GPS	IGPS	CS
$U_{\rm exp}~({\rm eV})$	1.50	1.52	1.51	0.25	1.60	1.70
ℓ (Å)	2.22	2.27	2.40	2.24	2.45	2.28
$\omega_{v} (\mathrm{cm}^{-1})$	517	519	375	570	523	414

structure. As shown in Table I the cohesive energy, bond length and the vibrational frequency of the dimer is well reproduced due to fitting procedure only to the dimer.

3.2. Screened Harrison Scaling Method

The Harrison scaling method has been improved by Khan and Broughton (1989) followed by Laasonen and Nieminen (1990). In this method the Harrison scaling is used, but the potentials are terminated between the first and second neighbors. Since the potentials have non-zero values at the cutoff, a short ranged scaling function has been used to make the potential smoothly falling to zero at the cutoff. The hopping matrix elements are given as

$$h_{\alpha}(r) = h_{\alpha}(r_0) \left(\frac{r_0}{r}\right)^2 \frac{1}{\exp\{\mu(r - r_c)\} + 1},\tag{7}$$

where r_c controls the range of interactions and μ is an adjustable parameter. The repulsive potential is calculated in a similar manner as proposed by Tománek and Schlüter (1987). Laasonen and Nieminen (1990) have optimized Si clusters up to ten atoms using this method and found reasonable agreement with the *ab initio* Hartree-Fock results by Raghavachari (1986). The advantage of this method over the model of Tománek and Schlüter is that the number of bonds are calculated from the cutoff function to allow the binding energy calculation suitable for the molecular dynamics simulation. The drawback of this method is that it does not reproduce the *ab initio* structural phases of Si. We have not compared the results obtained in this method with those in the CP-GGA method.

3.3. Method of Sawada

In the empirical scheme of Sawada (1990), the screened Harrison scaling method has been improved. This method has been employed by Kohyama (1991) to study bulk structural phases of Si. In this method the hopping integrals are given by

$$h_{\alpha}(r) = \eta_{\alpha}(r_0) \frac{1}{r^{\nu}} \frac{1}{\exp\{\mu(r - r_c)\} + 1}.$$
(8)

The bulk parameters for $h_{\alpha}(r_0)$ in Eq. (5) are replaced by some fitting quantities $\eta_{\alpha}(r_0)$. The scaling laws are different for different hopping integrals. For example, for $h_{ss\sigma}(r)$, $h_{sp\sigma}(r)$, $h_{pp\sigma}(r)$ and $h_{pp\pi}(r)$, the ν values are 4, 3, 2 and 2, respectively.

The repulsive potential takes the same form as the hopping integrals,

$$\Phi(r_{ij}) = \left[a_0 - a_1(Z_i + Z_j)\right] \frac{1}{r_{ij}^5} \frac{1}{\exp\{\mu(r - r_c)\} + 1},\tag{9}$$

where a_0 and a_1 are two fitting parameters and Z_i is the effective coordination number of the atom *i* and is given by

$$Z_{i} = \sum_{i \neq j} \exp\{-\lambda_{1}(r_{ij} - R_{i})^{2}\},$$
(10)

where R_i is given by

$$R_i = \frac{\sum_{j \neq i} r_{ij} \exp\{-\lambda_2 r_{ij}\}}{\sum_{j \neq i} \exp\{-\lambda_2 r_{ij}\}}.$$
(11)

Here λ_1 , λ_2 are two fitting parameters. This shows that the repulsive potential takes the environmental correction into account. Therefore the bond correction energy term is not necessary in this case.

The cohesive energies obtained in this way are shown in Fig. 2. From Fig. 2 it is quite clear that cohesive energies in this method are very small compared to the CP-GGA method. We also find that bond lengths are very large for all clusters. In Table I we find that the dimer bond length is very large and the vibrational frequency is very small compared to the experiment.

3.4. Goodwin, Pettifor and Skinner (GPS) Scaling

In the method of Goodwin *et al.* (1989) the discontinuity of the hopping integrals at the cutoff between the first and second neighbors is smoothed by exponential type functions,

$$h_{\alpha}(r) = h_{\alpha}(r_0) \left(\frac{r_0}{r}\right)^2 \exp\left[2\left\{-\left(\frac{r}{r_c}\right)^{n_c} + \left(\frac{r_0}{r_c}\right)^{n_c}\right\}\right].$$
(12)

The repulsive potential also takes the same form as the hopping integrals,

$$\phi(r) = \phi(r_0) \left(\frac{r_0}{r}\right)^{4.54} \exp\left[4.54\left\{-\left(\frac{r}{r_c}\right)^{n_c} + \left(\frac{r_0}{r_c}\right)^{n_c}\right\}\right].$$
(13)

The environmental correction is not considered in this method. The drawback of this method is that the binding energy of the FCC structure is lower than the BCC structure which contradicts the *ab initio* results.

This method has been applied by Lee *et al.* (1994) to study Si clusters up to 18 atoms. We find that the geometries of the medium sized clusters do not agree with the *ab inito* results. Therefore we have calculated the cohesive energies with our optimized

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geometries using this method. In Fig. 2 we find that the cohesive energies obtained using this method are too small compared to the CP-GGA method. The energy due to bond correction E_{bc} is not included in this calculation. We therefore do not agree with the results of Lee *et al.* (1994) and emphasize that without the E_{bc} term, it is not possible to obtain reasonable cohesive energies. The energies due to the charge transfer between atoms is too small to account for the large discrepancy of the cohesive energies from the CP-GGA method.

3.5. Improved GPS Model

Kwon *et al.* (1994) have taken the GPS form for the hopping integrals described in Eq. (12) with different r_c and n_c for different Slater–Koster matrix elements. The repulsive energy in this method is represented as

$$E_{\rm rep} = \sum_{i} f\left(\sum_{j} \Phi(r_{ij})\right).$$
(14)

The form of $\Phi(r_{ij})$ is the same as in Eq. (13) and $f(x) = d_1x + d_2x^2 + d_3x^3 + d_4x^4$ with d_1 , d_2 , d_3 and d_4 being adjustable constants. The environmental correction is taken in the embedded-atom approach to reproduce cohesive energies. This method reproduces the bulk properties, defects and clusters up to 5 atoms reasonably well. However, there are two drawbacks in this method. The clathrate structure has lower energy than the diamond structure. The cohesive energies calculated using this method without the energy of the isolated atom are shown in Fig. 2. We find that this model overestimates the cohesive energies compared to the CP-GGA method. In Table I we find that the bond length and vibrational frequency of the dimer are overestimated in this method.

3.6. Fractional Bond Model

Luo *et al.* (1999) have presented the fractional bond model for obtaining hopping integrals in an orthogonal tight binding description. The hopping integrals depends on several parameters related to bonding in a given system such as the number of bonding electrons, number of bonds and bonding strength per atom. The repulsive potential is assumed to depend on the position in an exponential manner. Unlike all other tight binding methods described before where the environmental correction is taken in the repulsive potential, this method takes this correction in the hopping matrix elements only.

We have tested this method for optimizing Si clusters and to our surprise we could not reproduce results reported by Luo *et al.* (1999). We suspect that the values of some parameters reported in this paper are misprinted.

3.7. Semi-Empirical Method of Mercer and Chou

The method of Mercer and Chou (1993) is the first semi-empirical method where the two-center hopping integrals and the repulsive potential are obtained by fitting to the valence electronic eigenvalues of the *ab initio* pseudopotential methods. The hopping

integrals have the same form as in Sawada method given in Eq. (8). The parameter ν is taken between 2.5 and 3.1 which are different than those taken by Kohyama (1991). The parameters η_{α} are smaller compared to those taken by Kohyama. These parameters do not make the potentials strongly position dependent as in the method of Kohyama (1991). The repulsive potential considers the environmental correction in a very complicated manner. The *ab initio* structural phases are reproduced in this method. Mercer and Chou (1993) have found the cohesive energies of Si₂ and Si₃ as 1.85 and 3.6 eV, respectively. We have not considered this method in the present work as the binding energies are somewhat overestimated.

3.8. Model of Lenosky

The complex form of the hopping integrals obtained from *ab initio* methods do not work well when they are fitted to some functional form (Bernstein *et al.* 1993). Lenosky *et al.* (1997) have represented the hopping integrals and the repulsive potential in the cubic splines, thus allowing only numerical procedures to perform molecular dynamics simulation. The potentials are obtained by carefully fitting to a data set consisting of *ab initio* energy and force as well as experimental data. Unlike other tight binding methods, the interaction cutoff is chosen up to fourth order distance in diamond structure. Also, the repulsive interaction included corrections due to many-body interactions not present in a pair potential model. This is supposed to be the only model to reproduce *ab initio* bulk phases, bulk physical parameters, defects and clusters up to five atoms better than any other tight binding method. The environmental correction is not necessary in this method.

The cohesive energies calculated using this method shown in 2 are found to be in excellent agreement with the CP-GGA method. Using this method Panda *et al.* (2001) have calculated bond lengths, fragmentation spectra, gap energies, Mulliken charges, dipole moments and static polarizabilities in Si clusters up to n = 19. In Table I we find that the cohesive energy and bond length of the dimer are in good agreement with the CP-GGA method. The vibrational frequency of the dimer is in good agreement with the non-orthogonal tight-binding method by Menon and Subbaswamy (2001).

4. CONCLUSIONS

In the present work we have compared cohesive energies of small Si clusters up to nineteen atoms using different orthogonal tight-binding schemes with the first principles CP-GGA method. The methods based on the short-range radial form of the matrix elements and repulsive potential overestimate the cohesive energies and bond lengths. The inclusion of the environmental correction in the repulsive part is essential for getting reasonable cohesive energies. On the other hand the matrix elements and repulsive potential calculated with radial cutoff up to fourth neighbor distance in diamond structure have correctly described cohesive energies and bond lengths without any environmental correction. In spite of the significant success of this model, the matrix elements $h_{ss\sigma}$ and $h_{pp\sigma}$ are seen to change sign which is not physically understood. This raises doubts about the transferability of the potentials in the orthogonal tightbinding schemes which paves way for the non-orthogonal tight-binding methods to be more meaningful for Si cluster studies (Menon and Subbaswamy (1997); Bernstein et al. (1993)).

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