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Nonorthogonal tight-binding molecular-dynamics scheme for silicon with improved transferability

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A previously proposed [Phys. Rev. B **50**, 11 577 (1994)] generalized tight-binding theory for silicon incorporating explicit use of nonorthogonality of the basis is modified to improve transferability. Better agreement is obtained over the original scheme for bond lengths, high-pressure bulk phases, and vibrational frequencies. [S0163-1829(97)03716-8]

I. INTRODUCTION

The computational efficiency of the tight-binding method derives from the fact that the Hamiltonian can be parametrized. Furthermore, the electronic structure information can be easily extracted from the tight-binding Hamiltonian, which, in addition, also contains the effects of angular forces in a natural way. Recently, several groups have proposed transferable tight-binding models for Si that attempt to give good agreement in the range all the way from a few atoms to the condensed solid, including many high-pressure bulk phases.[1–6] All these schemes, with the exception of Refs. 4 and 5, make use of orthogonal basis sets for parametrization. Consequently, they require a large parameter base to obtain good agreement for bulk phases. Additionally, none of the orthogonal schemes have reported comparisons with *ab initio* results for Si_N clusters with $N \geqslant 7$. The structure and stability determination for these clusters pose a severe challenge on account of the high coordination and low symmetry of these clusters. The orthogonal schemes also tend to give poor frequency estimates for Si clusters.

In a recent paper,[4] we introduced a transferable nonorthogonal tight-binding scheme for Si containing only three *adjustable* parameters, and a simple exponential distance dependence for the parameters, with no artificial cutoff in the interactions. The presence of so few adjustable parameters made the fitting procedure rather straightforward. The parameters were fitted to experimental bond lengths and vibrational frequencies of dimer and the bulk diamond structure in such a way as to minimize errors at both ends. Application of the formalism to small Si clusters in the range up to $N=10$ gave excellent agreement with *ab initio* results[7,8] for structures, cohesive energies, and frequencies. The scheme was also used to obtain the lowest-energy structure for the Si_{45} cluster,[9] in very good agreement with local-density approximation (LDA) based results.[10] Although structural and vibrational properties of the bulk diamond phase were well reproduced and the clathrate structure was found to be higher in energy than the diamond structure, the binding-energy differences between the high-pressure metallic phases and the diamond phase were overestimated. This was attributed to the simple distance dependence in the parameters and the use of only three adjustable parameters. In a recent work, Bernstein and Kaxiras[11] obtained improved agreement for high-pressure phases of silicon by fitting the same functional form of Ref. 4 to a database of first-principles total-energy calculations. This required varying all the universal matrix elements that were taken to be fixed in Ref. 4 and adding a few more parameters.

In this paper we present a small modification of our original scheme that greatly improves the agreement for the metallic phases of bulk Si while still maintaining good results for structural properties of Si clusters of arbitrary sizes. Additionally, improvement is also obtained for the cluster frequencies. This has been achieved by an alteration of the functional form of the nonorthogonality coefficient and the addition of only one adjustable parameter, while maintaining the simplicity of the original scheme.

In the following section we detail the changes in the formalism of Menon and Subbaswamy[4] (MS) that lead to overall improvements in many areas.

II. TECHNIQUE

The details of the technique can be found in Ref. 4. Here we give a brief summary and detail the modifications in the formalism.

In the nonorthogonal tight-binding scheme the characteristic equation for obtaining the eigenvalues is given by

$$(\mathbf{H}-E_n\mathbf{S})\mathbf{C}^n=0, \tag{1}$$

where **H** and **S** are the Hamiltonian and overlap matrices, respectively.[4,12]

The Hellmann-Feynman theorem for obtaining the electronic part of the force is given by[4]

$$\frac{\partial E_n}{\partial_x}=\frac{\mathbf{C}^{n\dagger}\left(\frac{\partial \mathbf{H}}{\partial}-E_n\,\frac{\partial \mathbf{S}}{\partial x}\right)\mathbf{C}^n}{\mathbf{C}^{n\dagger}\mathbf{S}\mathbf{C}^n}. \tag{2}$$

In the Slater-Koster scheme the Hamiltonian matrix elements are obtained from the parameters $V_{\lambda\lambda'\mu}$ in terms of the bond direction cosines l,m,n.[4,13,14] In the MS scheme the parameters $V_{\lambda\lambda'\mu}(r)$ are taken to decrease exponentially with r:[4]

$$V_{\lambda\lambda'\mu}(r)=V_{\lambda\lambda'\mu}(d_0)e^{-\alpha(r-d_0)}, \tag{3}$$

where d_0 is the sum of the covalent radii of the pair of interacting atoms and α is an adjustable parameter. The scaling of the repulsive term is also taken to be exponential:

$$\phi(r)=\phi_0 e^{-\beta(r-d_0)}, \tag{4}$$

where $\beta=4\alpha$.[4]

In the nonorthogonal scheme, the overlap matrix is calculated in the spirit of extended Hückel theory[15] by assuming a proportionality between **H** and **S**:[12]

$$S_{ij}=\frac{2}{K}\frac{H_{ij}}{H_{ii}+H_{jj}}. \tag{5}$$

The diagonal elements of H_{ij}, as in the orthogonal theory, are taken to be the valence s and p energies. The off-diagonal interatomic matrix elements are given in terms of the Hamiltonian matrix elements in orthogonal theory (V_{ij}) by

$$H_{ij}=V_{ij}\left[1+\frac{1}{K}-S_2^2\right], \tag{6}$$

where

$$S_2=\frac{(S_{ss\sigma}-2\sqrt{3}S_{sp\sigma}-3S_{pp\sigma})}{4} \tag{7}$$

is the nonorthogonality between sp^3 hybrids.[12] Note that the original MS scheme [Ref. 4, Eq. (10)] contained an extra term in the definition of S_2 that has been dropped in the present work. The quantities $S_{\lambda\lambda'\mu}$ in turn are determined from

$$S_{\lambda\lambda'\mu}=\frac{2V_{\lambda\lambda'\mu}}{K(\varepsilon_\lambda+\varepsilon_{\lambda'})}. \tag{8}$$

We take a simple exponential distance dependence in the nonorthogonality coefficient K

$$K(r)=K_0e^{\sigma(r-d_0)^2}. \tag{9}$$

In the original MS scheme this distance dependence was algebraic and, $\sigma=\alpha$ [see Eq. (14) of Ref. 4]. As shown later, this exponential dependence yields better transferability by improving results for the high-pressure metallic phases of bulk Si. This approach is similar in spirit to Anderson's[16] modification to the extended Hückel method. This improvement is perhaps not surprising if one considers the fact that the algebraic expression for $K(r)$ in Ref. 4 is simply one of the terms in the expansion of $K(r)$ in Eq. (9), and we have introduced an additional parameter, namely, σ.

In Table I we list all the parameters used for Si.

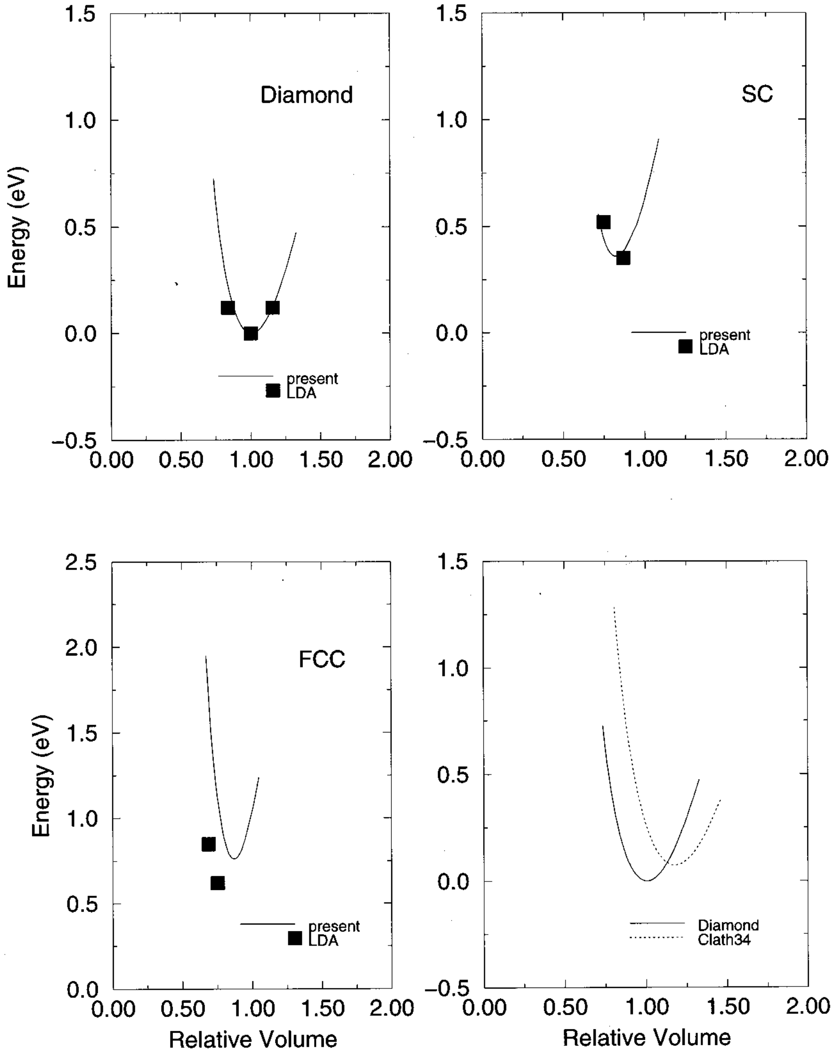

FIG. 1. The cohesive energies of various structures of silicon using the present scheme. The filled squares are LDA results.

TABLE I. Parameters used in the present scheme for silicon.

A priori parameters			Adjustable parameters			
ϵ_s (eV)	ϵ_p (eV)	d_0 (Å)	α (Å^{-1})	K_0	χ_0 (eV)	σ (Å^{-2})
−13.55	−6.52	2.36	1.62	1.7	0.41	2.5

III. RESULTS

A. Solid

In this section we present our results obtained using the modified nonorthogonal scheme. All the results are obtained without introducing any artificial cutoff in the interactions. In practice this is achieved by increasing the shell size until results remain unchanged. This implies inclusion of up to the third-neighbor shell (corresponding to a cutoff of 5.5 Å).

Figure 1 shows the zero-temperature phase diagram for silicon obtained by our method. The high-pressure phases (fcc, sc) are vastly improved over the original results in Ref. 4. In computing the electronic energies special point integrations were performed and tested for convergence. As can be seen in the figure, the diamond structure is lowest in energy even when compared with the clathrate structure with the same coordination, with a difference in energy of 0.07 eV/atom.

The force constants for the evaluation of vibrational modes are obtained by employing analytic second derivatives of the electronic structure. Hamiltonian matrix elements.[19] This method, while providing better accuracy than conventional schemes, greatly expedites the determination of vibrational modes for large size clusters. The vibrational frequencies at some symmetry points are given in Table II. Both the acoustic and optic branch phonons are in excellent agreement with experiment, with a maximum mode deviation of only up to about 13% from experiment.[21] This should be contrasted with the best orthogonal schemes that achieve agreement to only within 45% while using many more parameters.[3] As shown in the next section on clusters, the same scheme gives a reasonable vibrational frequency for the symmetric stretch mode for the dimer.

B. Clusters

We next briefly describe our results for small silicon clusters using the present scheme. All geometries were optimized by molecular-dynamics relaxation using precisely the same tight-binding parameters. As in the original scheme, no cutoff is used in the present calculations and no coordination-dependent term is needed for cohesive energy estimates. In Table III we give binding energies of the most stable clusters. In comparing our *absolute* cohesive energies with *ab initio* results, a constant shift of 1.1 eV to our computed values brought all values into excellent agreement.

TABLE II. Comparisons showing transferability for silicon. The numbers in parentheses are experimental values.

	Bond length (Å)	Vibrational frequency (cm^{-1})
Si (dimer)	2.22 (2.24)[a]	422 (517)[b]
Si (diamond)	2.36 (2.35)[a]	$\Gamma_{\mathrm{TO}}=586$ (517)[b] $L_{\mathrm{LO}}=455$ (417)[b] $L_{\mathrm{LA}}=367$ (368)[b] $X_{\mathrm{LO}}=524$ (463)[b] $X_{\mathrm{TO}}=429$ (414)[b]

[a] Reference 20.

[b] Reference 24.

TABLE III. Cohesive energies (in eV/atom) for Si_N clusters. Our computed values were shifted up uniformly by 1.1 eV to bring absolute values into agreement with *ab initio* values.

		Binding energy (eV/atom)	
N	Symmetry	*ab initio*[a]	Present work
2		1.56	1.55
3	C_{2v}	2.54	2.48
4	D_{2h}	3.17	3.13
5	D_{3h}	3.3	3.36
6	C_{2v}	3.6	3.63
7	D_{5h}	3.8	3.81
8	C_{2h}	3.65	3.78
9	C_{3v}		3.90
10	C_{3v}	3.82	3.99

[a] Reference 8; note that the C_{3v} structure for $N=9$ was not considered (see text).

For Si_2, we obtain a dimer bond length of 2.22 Å and a vibrational frequency of 422 cm^{-1}. The corresponding experimental values are 2.24 Å and 517 cm^{-1}, respectively. In Table II we compare our results with experiment for bond lengths and vibrational frequencies at the dimer and bulk ends to illustrate the transferability of the present scheme.

The ground-state structural results for all clusters, with the exception of Si_9, are in complete agreement with *ab initio* values.[8] For the Si_9 cluster, as in Ref. 4, we find a distorted tri-capped trigonal prism (C_{2v} symmetry, proposed by Ordejòn, Lebedenko, and Menon[21]) to be the ground state. More recent *ab initio* calculations[21] using an unrestricted Hartree-Fock calculation with 6-31 G^* basis including correlation effects have also suggested this structure to be the ground state.

In Table IV we compare the results for vibrational frequencies for the Si_7 cluster (pentagonal bipyramid, D_{5h} symmetry), with the corresponding *ab initio* values.[8] As can be seen, the overall agreement is good, confirming the validity of the present scheme for frequency estimates for Si clusters of arbitrary sizes.

Application of the present scheme to the Si_{45} cluster yields lowest-energy isomers that consist of two concentric shells with a highly distorted fullerenelike outer layer, and a highly coordinated inner core with a central atom.[9] Our re-

TABLE IV. Vibrational frequencies for the Si_7 cluster.

	a_1'	e_1'	e_2'	a_2''	e_1''	e_2''
Present work	322 517	234 482	217 378	358	340	130
ab initio[a]	384 439	250 430	271 370	241	346	146

[a] Reference 8.

sults agree with LDA-based results that suggest these geometries for the low-energy isomers for the Si_{45} cluster.[10]

Transferability from solid to cluster is crucial to the study of crystal growth. Clusters with $N \geqslant 7$ are particularly challenging on account of the high-coordination and low-symmetry geometries predicted by *ab initio* calculations[8] for these clusters. We note that orthogonal tight-binding schemes have found it necessary to introduce an *ad hoc* coordination-dependent term to get reasonable agreement with *ab initio* values for cohesive energies.[22,23]

IV. DISCUSSION AND SUMMARY

We have presented an improved version of the transferable generalized tight-binding scheme for silicon that incorporates the overlap interactions explicitly, and obtained agreement on a wide range of properties for different phases. The simplicity of the original formalism is retained and only one additional parameter has been added. The most notable improvements have been in the area of high-pressure metallic phases and the vibrational frequencies. While previous attempts at constructing transferable tight-binding schemes[1–3] have had some success, the number of adjustable parameters required had to be increased considerably. We believe this to be the result of the implicit assumption of orthogonality of the atomic basis in the formalism.

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