

Tight-binding model with intra-atomic matrix elements

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We present a tight-binding model for silicon which incorporates two-center intra-atomic parameters. The model is fitted to density-functional theory band structures for silicon in the diamond structure over a number of volumes. It is shown that with only a two-center, orthogonal basis, reasonable total energies can be obtained for many different structures. Thus it eliminates the need to use structure-dependent terms in the total-energy model.

Tight-binding (TB) total-energy models have been widely used for the study of complex systems in which the large number of atoms per unit cell prohibits first-principles calculations. In many cases, these semiempirical models achieve results which closely parallel experimental and *ab initio* values.¹⁻⁴ The TB basis functions, in their simplest form, are assumed to be orthogonal and the matrix elements are often approximated by two-center integrals. In a recent study,⁴ we found the distance dependence of the two-center matrix elements for silicon and germanium by fitting the TB parameters to band structures at different volumes obtained from density-functional-theory (DFT) calculations within the local-density approximation. A repulsive potential, which takes the form of a pairwise interaction multiplied by a *structure-dependent* function, is added to the TB sum of eigenvalues in order to reproduce the total energies for a number of bulk structures.⁴ It is clear that transferable, orthogonal two-center tight-binding models based on DFT distance dependence have to contain some terms describing the local environment. This conclusion is consistent with work which found that orthogonal parameters fitted to one structure (and coordination) could not be transferred to another structure (and coordination) without an extra term,⁵ a term which could be given by a structure-dependent function.

In this work, we will examine an alternate approach which removes the need for a structure-dependent function by including intra-atomic parameters explicitly in the tight-binding total-energy formulation for silicon. These two centered parameters^{2,6-8} are generally structure dependent. To illustrate the usefulness of these parameters, we show that, in addition to the one-electron energy sum, only a two-body pair potential is needed to create a binding-energy model that is sufficient to give reasonable fits to other crystalline forms of silicon.

A typical binding-energy formulation includes the tight-binding band energy sum (E_{bs}) plus a classical repulsive term (E_{rep}). E_{bs} is the sum of the occupied eigenvalues of the band structure while E_{rep} is a correction term for the ion-ion interaction and the overcounting of the electron-electron interaction. By using the station-

ary principle with an appropriate input density, it can be shown that this semiempirical energy expression can be obtained from DF theory.⁸ The cohesive energy can be written as

$$E_c = E_{bs} + E_{rep} - E_0, \quad (1)$$

where E_0 is the energy of an isolated atom. The E_{bs} can be based on *ab initio* work by adjusting the tight-binding parameters so as to fit the *ab initio* eigenvalues. If this is done over a wide range of nearest-neighbor distances for tetrahedral silicon and combined with an appropriate E_{rep} , then the *ab initio* binding energy for tetrahedral silicon is reproduced. When this model is applied to other crystalline forms such as β -tin, simple cubic (sc), body centered cubic (bcc), and face centered cubic (fcc) the results are rather poor. Schilfsgaarde and Harrison have argued that these results are because an orthogonal TB fit to tetrahedral structures does not transfer correctly to other structures.⁵ An appropriate method would be to include nonorthogonal terms as Sigalas and Papaconstantopoulos have done for iridium.⁹ By fitting the nonorthogonal tight-binding parameters and repulsive potential to two forms of iridium they produce a model which gives reasonable results when transferred to other iridium structures.

Alternatively, the transferability could be increased by the use of a structure-dependent function in the repulsive term. In this case, it would seem necessary to include in E_{rep} some factor which would allow a better fit to other crystalline forms. An example of such a model was given for silicon and germanium.⁴ In the model, E_{rep} was

$$(E_{rep})_i = \omega \sum_j \Phi(r_{ij}). \quad (2)$$

Here Φ is a pairwise interaction while ω is a structure-dependent function included to reproduce other crystalline energies. The most complicated part of E_{rep} is the formulation of ω ; its removal would be a useful simplification both conceptually and computationally.

It is possible to produce a strictly two-body TB model which describes more than one structure such as Goodwin, Skinner, and Pettifor¹⁰ have done. In their model,

the tight-binding distance dependence, together with the parameters in E_{rep} , is treated as a fitting parameter. Here we wish to show that using the DF values for the TB parameters and thus the DF distance dependence, we can reproduce very well the energies and volumes of other structures from a two-body transferable model when the intra-atomic tight-binding parameters are included.

The standard nearest-neighbor, orthogonal, two-center, tight-binding analysis for silicon includes six parameters. Two are the on-site energy parameters E_s and E_p which give the energy for the s - s state and p - p state interactions when both interacting orbitals are located on the same atom. These are assumed constant when strictly speaking they depend upon local environment.⁶ $H_{ss\sigma}$, $H_{sp\sigma}$, $H_{pp\sigma}$, and $H_{pp\pi}$ are the other four two-center parameters.¹¹ Since most systems of interest involve some deviation from the fitted case, the H parameters are given some distance dependence and combined with an angular dependence from Slater and Koster¹¹ to give the final matrix elements.

Within the nearest-neighbor two-center approximation, E_s actually depends on the structure⁶

$$(E_s)_i = s_0 + \sum_j I_{ss\sigma}(r_{ij}) = s_0 + (I_s)_i, \quad (3)$$

where s_0 is the atomic energy and $I_{ss\sigma}(r_{ij}) = \langle s_i | V_j | s_i \rangle$ is the additional interaction from the crystal and is summed over the nearest neighbors. When all the atoms are equivalent in a crystal, E_s can be written as a constant. If even one of the neighbors were to move then conceivably the value of $I_{ss\sigma}$ would change and so would E_s . E_s would also change if the number of nearest neighbors changed. Away from the environment for which it was fitted, E_s as a constant would very likely be incorrect. E_p follows a similar pattern.⁶ E_{p_z} , for example, can be written as

$$\begin{aligned} (E_{p_z})_i &= p_0 + \sum_j [l_{ij}^2 I_{pp\sigma}(r_{ij}) + (1 - l_{ij}^2) I_{pp\pi}(r_{ij})] \\ &= p_0 + (I_{p_z})_i. \end{aligned} \quad (4)$$

Here l_{ij} , m_{ij} , and n_{ij} are the direction cosines.¹¹ For simplicity, the sum over neighbors in E_s and E_p is written as I_s and I_p , respectively. Thus, the parameters E_s and E_p which are usually taken as constant are now open to distance and coordination dependence through $I_{ss\sigma}$, $I_{pp\sigma}$, and $I_{pp\pi}$. E_0 now equals $2(s_0 + p_0)$. There are additional parameters such as

$$\langle p_{x,i} | H | p_{y,i} \rangle = \sum_j l_{ij} m_{ij} [I_{pp\sigma}(r_{ij}) - I_{pp\pi}(r_{ij})] \quad (5)$$

and

$$\langle p_{x,i} | H | s_i \rangle = \sum_j l_{ij} I_{sp\sigma}(r_{ij}). \quad (6)$$

For tetragonal, cubic, and hexagonal crystals these latter terms sum to zero.⁶ Therefore $I_{sp\sigma}$ cannot be determined from the crystalline data available for Si. We have neglected it in the present study. It should be noted that the value of E_s and hence E_p is altered in some studies

so as to provide local charge neutrality.^{10,12} However, local charge neutrality is not a concern in ordered crystals and this technique which implicitly alters $I_{ss\sigma}$, $I_{pp\sigma}$, and $I_{pp\pi}$ to guarantee charge neutrality would have no effect in the crystal.

To test the effectiveness of using the parameters I , the DF band structure of tetrahedral silicon was fitted by nearest-neighbor, orthogonal parameters. The parameters E_s and E_p (diagonal elements) were allowed to vary independently of each other over the fourteen volumes considered (equivalent to nearest-neighbor distances ranging from 2.14 to 2.91 Å which covers nearest-neighbor distances up to and including fcc). The H parameters were fitted to distance dependent functions of the form

$$H(r) = \alpha r^{-\beta} e^{\mu r}. \quad (7)$$

The values for α , β , and μ for the different interactions are given in Table I. In Fig. 1, the four H parameters are compared to the previous fitting⁴ and to a $\frac{1}{r^2}$ scaling. The difference between the previous fit (no I) and this fit shows the effect of letting E_s and E_p vary with distance. $H_{pp\sigma}$ and $H_{pp\pi}$ do not differ much from the previous fit while both $H_{ss\sigma}$ and $H_{sp\sigma}$ tend to fall off less rapidly with distance. Since this is associated with the increase in distance dependence of E_s and E_p , it is quite likely that the s orbital interactions with no I parameters were partially absorbing the behavior of the I parameters.

The distance dependence of E_s and E_p in the diamond structure is shown in Fig. 2. $I_{ss\sigma}$ can be obtained from E_s using Eq. (3), while E_p provides $I_{pp\sigma}$ and $I_{pp\pi}$ only in a combined form given by Eq. (4). The combination depends on the type of structure we have. For the cubic structures (diamond, sc, bcc, and fcc), the ratio of $\sum_j l_{ij}^2$ to $\sum_j (1 - l_{ij}^2)$ is the same. Therefore the combination could be transferred as E_p to other cubic structures without the individual knowledge of $I_{pp\sigma}$ and $I_{pp\pi}$. For a structure like β -tin, it is necessary to know $I_{pp\sigma}$ and $I_{pp\pi}$ individually and this can be found from the fitting of ei-

TABLE I. Parameters for silicon obtained from fitting to the band structure and total energy of *ab initio* calculations.

	α (eV/Å ⁶)	β	μ (Å ⁻¹)
$V_{ss\sigma}$	-44.693	7.176	-4.022
$V_{sp\sigma}$	18.090	5.478	-2.957
$V_{pp\sigma}$	27.692	-3.121	0.0
$V_{pp\pi}$	-31.090	-0.792	-1.107
	$I_{ss\sigma}$	$I_{pp\sigma}$	$I_{pp\pi}$
a_0 (eV)	35.035	-77.566	138.198 eV
a_1 (eV/Å)	-89.837	101.589	-238.361
a_2 (eV/Å ²)	73.907	-43.723	153.546
a_3 (eV/Å ³)	-24.943	6.269	-43.971
a_4 (eV/Å ⁴)	2.998	0.0	4.728
a_5 (eV)	0.25	1	1
a_6 (Å)	30	30	30
a_7 (Å)	2.0	2.0	2.0
	Φ		
b_0	-2631.478 eV		
b_1	5414.843 eV/Å		
b_2	-4333.996/Å ²		
b_3	1692.506/Å ³		
b_4	-322.919/Å ⁴		
b_5	24.267/Å ⁵		
b_6	-0.069/Å ⁶		

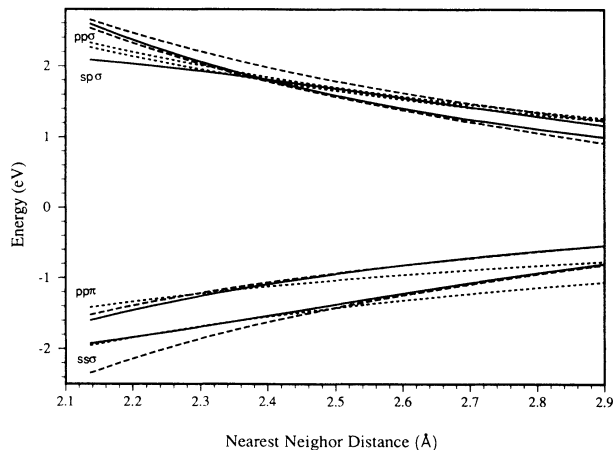


FIG. 1. A comparison of the distance dependence of tight-binding parameters. The solid lines are for the present fitting which includes the intra-atomic matrix elements, while the dashed lines are for an identical fitting (Ref. 4) without the intra-atomic matrix elements. The dotted line shows the $\frac{1}{r^2}$ behavior.

ther the total energy or the band structure to DF results of such a structure.

We give the intra-atomic parameters $I_{ss\sigma}$, $I_{pp\sigma}$, and $I_{pp\pi}$ here and describe below how we obtained these forms. The final form is

$$I_{ss\sigma} = a_0 + a_1 r + a_2 r^2 + a_3 r^3 + a_4 r^4 + a_5 e^{a_6(a_7 - r)}. \quad (8)$$

$I_{pp\pi}$ has the same form while $I_{pp\sigma}$ lacks the r^4 term. $I_{sp\sigma}$ is not given since it does not affect crystalline results, but can serve as a further parameter for noncrystalline and surface work.

Using the values obtained for H and I parameters above and *ab initio* total-energy values for diamond, the two-body repulsive potential, $(E_{\text{rep}})_i = \frac{1}{2} \sum_j \Phi(r_{ij})$, could be determined. $\Phi(r)$ was fitted to a polynomial as

$$\Phi(r) = b_0 + b_1 r + b_2 r^2 + b_3 r^3 + b_4 r^4 + b_5 r^5 + b_6 r^6 \quad (9)$$

and is shown in Fig. 2. This total-energy model was then

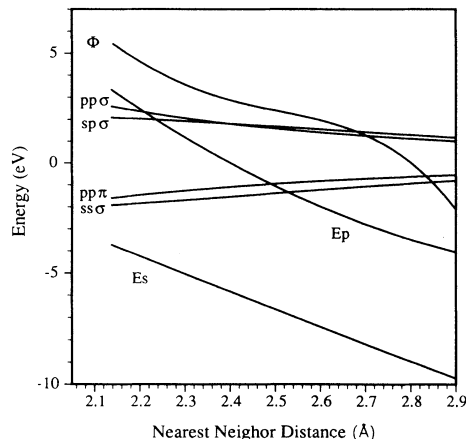


FIG. 2. The distance dependence of E_s and E_p obtained from the diamond structure compared with the H parameters. The repulsive potential Φ is also shown.

used for the other crystal structures. The results for all structures along with the DFT results are shown in Fig. 3.

The results for the cubic structures are good. Diamond being the fitting structure is certainly good, while the sc and fcc results indicate that no three-body terms and no structure-dependent E_{rep} are necessary in order to reasonably reproduce these structures. bcc which had a reasonable equilibrium volume came out too high in energy (by 0.3 eV) to be shown. Further investigation pointed to at least some of the error in bcc being due to small fitting errors for the TB parameters in the region of the bcc nearest-neighbor distance. It is also possible that the increased importance of nonorthogonality for this closely compacted structure is a source of error.¹³ Since bcc is not of much importance we do not pursue this further at this point. The remaining three structures shown, β -tin,¹⁴ bc8,¹⁴ and bct5,^{15,16} are also reproduced quite well. Each required a minimum amount of information concerning $I_{pp\sigma}$ and $I_{pp\pi}$. Since E_p could be divided between $I_{pp\sigma}$ and $I_{pp\pi}$ in many ways with good results, these structures did not have much influence on the final form of the I parameters.

The final form was dictated by drawbacks to the E_s and E_p (and therefore the I) parameters as given by the DF fitting. In addition to the bulk structures, we tested phonons, shear modulus, and the two-atom molecule Si_2 . The drawbacks, in particular, were that the dimer tended to shrink to very small bond lengths and at least one of the phonons [LOA(X)] was very poorly described. After study of the DF information for the phonons and the dimer, it became evident that the disagreement was due to the absence of either three-body terms or second-nearest neighbors. Specifically, the $I_{ss\sigma}$ values obtained

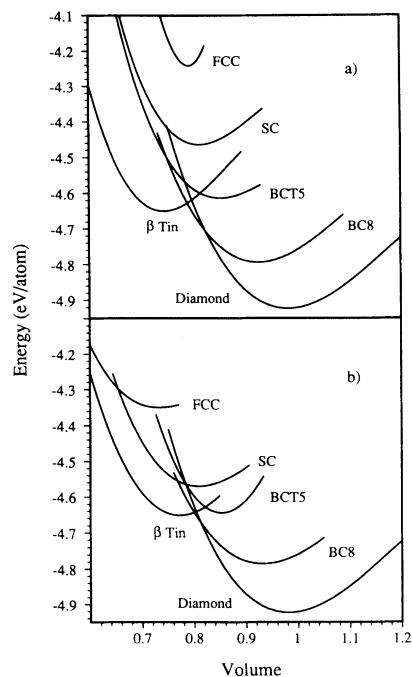


FIG. 3. (a) The binding energies for the structures using the final values for the I , H , and E_{rep} terms. (b) The same structures as given by DFT calculations (Refs. 14–16 and 18).

TABLE II. Phonon values for silicon compared to a previous fitting (Ref. 4) and to DFT (Refs. 18 and 19). Frequencies are in THz.

	Present model	Previous fitting	DFT
LTO(Γ)	15.8	14.7	15.2
LAO(X)	11.2	11.2	12.2
TO(X)	13.0	14.4	13.5
TA(X)	3.58	4.5	4.45

from the perfect diamond crystal did not give the correct change of the on-site parameter E_s in the phonon calculation as compared with the results of a TB fitting of the DF eigenvalues for the phonon. This was also true of Si_2 . Within the first-nearest-neighbor approximation, this difference in E_s would lead us to the conclusion that a three-body term is actually necessary. However, it might also be possible to fix the problem by including the second-nearest neighbors. The E_s behavior for the phonons and Si_2 would certainly change with the second-nearest neighbors included.

If one stays within the two-center, nearest-neighbor approximation, these problems could be taken care of through a relaxation of the requirements that the I parameters accurately give E_s and E_p as described by DF fitting. The exponential function in the I formulations was added to reproduce the sharp rise in energy for small bond lengths seen for Si_2 . To correct the phonon energy, the large slope in the diamond nearest-neighbor region was decreased for each of the I 's. The final values, at the diamond nearest-neighbor distance (2.35 Å), for the TB parameters are (in eV) $E_s = -6.50$, $E_p = 3.20$, $I_{ss\sigma} = -0.874$, $I_{pp\sigma} = 1.069$, $I_{pp\pi} = -0.460$, $s_0 = -3.00$ and $p_0 = 3.00$. After the I parameters are determined, the two-body potential in Eq. (8) is recalculated.

Although it did move fcc and sc energies up slightly, overall the relaxation made little difference to the struc-

tural energies and volumes. This small difference indicates that it is important physically to include the I parameters while their particular values are not nearly as important. The dimer Si_2 bond length of 2.17 Å came out short, but the energy appears to be quite good. Dynamical results are listed in Table II. The phonons, with the exception of TA(X) agree very well with DF data. The value for the shear modulus ($c_{11} - c_{12}$) is also low being only half of what it should be (as is common among first-nearest-neighbor TB models which give good phonons¹⁷). In the future, we hope to add second-nearest neighbors and in so doing allow naturally for the two alterations mentioned above. In addition, the second-nearest neighbors should provide a better shear modulus.

The intra-atomic parameters $I_{ss\sigma}$, $I_{sp\sigma}$, $I_{pp\sigma}$, and $I_{pp\pi}$ can be used to add more *ab initio* information to a tight-binding model. The input data are the volume-dependent DF eigenvalues and total energies in the diamond structure. Additional qualitative information, due very possibly from the first-nearest-neighbor restriction, was needed from the on-site parameter and total-energy change in Si_2 and with phonon displacements. In general, the formulation improves significantly on the tight-binding energy model by both reducing the complexity of the repulsive potential and increasing transferability without the need for nonorthogonality of the TB parameters. Results for a number of structures and test cases showed strong agreement with *ab initio* data. The possible advantages of these extra parameters in noncrystalline cases are apparent.

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