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Tight-binding total energy models for silicon and germanium

James L. Mercer, Jr. and M. Y. Chou
School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332

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By accurately fitting tight-binding parameters to *ab initio* band structures from 14 different tetrahedral volumes, tight-binding parametric formulas have been developed for silicon and germanium. The distance dependences for these orthogonal, nearest-neighbor parameters range from $r^{-2.5}$ to $r^{-3.3}$. Repulsive potentials are added in order to reproduce the total energies for a number of bulk structures. It is found that the repulsive potential needed has the simple form of a pairwise interaction multiplied by a structure-dependent constant. Transferability is shown with good bulk and cluster results.

I. INTRODUCTION

Elemental semiconductors, particularly silicon, due to their technological importance have been the focus of much research. Understanding and predicting their properties has been the goal of a number of models that have been proposed. Classical potentials typically provide a quick analysis of a system. However, their transferability from one type of system to another is often questionable.[1] For the best accuracy, a fully quantum-mechanical treatment of the entire system is possible with *ab initio* calculations. These calculations carry the cost of extremely high computational demand as the number of atoms increases. One recent calculation of the Si(111) 7×7 surface required "several hundred hours" on a massively parallel computer.[2] There still exist systems that are too large to be handled by *ab initio* calculations. To study these systems, a tight-binding method augmented with a classical potential for the total energy will be most suitable.

The tight-binding (TB) calculation usually reduces the quantum-mechanical treatment to the valence electrons, the electrons which are involved in bonding. The technique which is discussed in more detail elsewhere[3] uses parametric representations of interactions so as to obtain approximate solutions to the electronic bonding behavior. Typically, these parametrizations are based on *ab initio* or experimental data. Calculations may range from first-nearest neighbor (NN), orthogonal, and valence orbitals (s and p for Si and Ge) only, to third nearest neighbor, d orbitals, and nonorthogonal sets.[4–9]

Early analysis[10] suggested a $\frac{1}{d^2}$ behavior for the tight-binding parameters. This was assumed based on the interpretation of experimental data compared to tight-binding calculations of various systems with different constants and also was derived by comparing tight-binding bands to free-electron calculations. Most previous parametrizations have used $\frac{1}{d^2}$ or no distance dependence. There are exceptions.[9,11–13] Notable among these is the tight-binding model for silicon based on pressure-dependent comparisons of tight-binding and *ab initio* work.[12] This work used two *ab initio* band structures, one under pressure and one at zero pressure, to determine the distance dependence for a five orbital model (sp^3s^*). Deviations from the $\frac{1}{d^2}$ behavior were quite noticeable. With some approximations this was reduced to sp^3 and used for a total energy model.[13] However, a detailed examination of the distance dependence of these parameters by comparing with the *ab initio* band structure has not been performed.

TB calculations only provide the electronic information, which is not sufficient to explain all of the bonding behavior; the ion-ion repulsion and a correction for overcounting of the electron-electron interaction are also needed. This extra information is quite often provided by a classical potential. One such potential[14,15] uses a linear and square term dependent on the change in the distance of bonds to provide the fitting. This scheme for Si has been widely used. For the bulk, there is also a bond-dependent term, while for surface calculations additional bond-dependent terms are needed. The values of the parameters for the extra terms are given by fitting to the energy of various surfaces as found from *ab initio* work.[16] A number of other repulsive potentials have been used with certain success.[17–20] Some recent TB total-energy models appear to give reasonable accuracy for a number of silicon structural phases.[11,13] In one case, the tight-binding parameters and the repulsive potential have been fitted simultaneously so that the total energy results are good.[11] However, when other crystal structures are tested, the transferability is not quite satisfactory.[21] The results indicate the importance of constructing a repulsive potential that depends on the local environment.[21]

In the present work, parameters that are required by a transferable total energy model are systematically studied. First, the band structures for silicon and germanium are fitted over a very wide range of compressions and expansions to *ab initio* results to determine the distance dependence of the interaction parameters. This represents a significant extension over previously published work for silicon, especially by the inclusion of expanded lattices. Such work for germanium seems to be completely new, having only been hinted at in previous silicon results.

For the ease of future applications in large systems, we consider only orthogonal orbitals with nearest-neighbor interactions. The distance dependence of these parameters is found to range from $r^{-2.5}$ to $r^{-3.3}$. Second, the appropriate form for the repulsive potential to reproduce the energy versus volume curve is investigated. A multiplying constant that depends on the local environment is found to be needed for the pairwise potential. The current total energy model for silicon gives improvements over other models. This paper is set up as follows: Sec. II deals with the development of the tight-binding parametrizations, Sec. III deals with the development of the repulsive potentials, and Sec. IV discusses a number of test cases and the transferability of the current parameters.

II. TIGHT-BINDING PARAMETERS

The emphasis for modeling the electronic structure of Si and Ge was placed on the most important form (tetrahedral) of the elements. In order to limit the complication of the fitting and further calculations using the parameters, it was decided to use an orthogonal basis set so as to reduce the number of matrices (no overlap matrix) and the complication of the eigenvalue problem. The parameters are determined by a fitting to the valence electronic eigenvalues found from *ab initio* calculations. The motivation for doing this comes from the fact that the *ab initio* results are usually in excellent agreement with experiment and many more k points are available from *ab initio* calculations than from experimental data. By accurately reproducing the *ab initio* band structure, the correct electronic contribution will be made to the binding energy. Furthermore, by using the *ab initio* results as the starting point, the self-consistency present in the *ab initio* calculations will be, to some extent, built into the new parameters.

The main objective was a distance dependence determined by the parameters. Instead of working with several different structures[9] or by using only one pressure point,[12] the distance dependence was found by calculating the parameters across 14 volumes (or pressures) for the tetrahedral structure and then fitting the change in the values to the change in distance. A calculation for fcc in silicon was also tried. These values will not be used in any of the following formulations. The decision to not use the fcc values was based in part on their reduced accuracy and on the fact that since the atomic orbitals are changed from their equilibrium state, the values of the orbital interactions differed from the tetrahedral values. Therefore, it is hoped that the effect of having a different local environment on the total energy can be absorbed later in the structure-dependent repulsive potential.

The NN distance examined ranges from 2.14 to 2.91 Å; this range was chosen so as to cover sufficiently small distances and to cover what some researchers[22] have found in amorphous silicon (via molecular-dynamics simulations) to be the largest distance for a first NN. These distances correspond to volumes that range from 75% of the experimental value to 190% of it. Within these boundaries, only first nearest neighbors for the tetrahedral structure exist, but for other structures second nearest neighbors exist and must be prevented from interacting. A cutoff function will take care of this.

In order to obtain a sufficiently accurate description of the valence bands the parameters were fitted for each volume to 13 k points. Three of these points, special high symmetry ones, are the Γ, X, and L points, and the other ten are the points that are commonly used in carrying out the Brillouin-zone summation for the diamond structure. Since the local-density approximation (LDA) does not produce an accurate band gap and the major concern here is the total energy, only valence bands are used in the fitting. The fitting then includes 52 eigenvalues from the *ab initio* calculations using norm conserving pseudopotentials.[23] As input the lattice length of each crystal was varied in accordance with the volume (or pressure) change.

The Ceperley-Alder (CA) exchange correlation[24] term for the silicon calculations and the Wigner correlation[25] for the germanium calculations were used. Other input such as the atomic pseudopotentials and the cutoff energy for the plane waves used in the calculations were taken from the work of Yin and Cohen.[26]

No distance dependence was forced thereby preventing any preference from weakening the results. Initially, six parameters were allowed to vary for each volume, those six parameters being $ss\sigma, sp\sigma, pp\sigma, pp\pi$, s_0, and p_0.[3] The freedom of s_0 and p_0 seemed to cause too many problems and trial and error was used to assign a value to the separation of these two. With this value set, five parameters were then calculated where the fifth value s_0 allowed for any reference level movement in the *ab initio* calculations; later this value was fixed, with the hope that the variations can be included in the repulsive potential term. The fittings were performed five times; the sets that produced smooth curves as a function of distance were used for the final distance dependence.

It was found that a poor choice for the s_0-p_0 separation would not only give bad results in fitting to certain volumes, but could also quite easily cause the Γ valence triply degenerate values to switch too soon with the conduction singly degenerate values. After trying a variety of energy values for the s_0-p_0 separation ranging in energy from 3 to 10 eV, 5.3 eV was found to be the largest value that still gave the correct ordering for the Γ triple and single in silicon. It was noticed that as this value increased the fitting for all but the very low volume set was improved, but the upper limit was set by the Γ behavior. For germanium s_0-p_0 is 6.2 eV. These separations for Ge and Si are towards the low end of their equivalent values from other determinations; for example, Chadi[14,15] gives values for s_0-p_0 to be from 5.9 to 7.2 eV for silicon (6.2 eV being the most widely used) and 7.35 to 8.41 eV for germanium, while another study[9] also gives 6.24 eV for silicon. The actual value of s_0 is of little importance due to the fact that the prime concern is cohesive energies and not absolute energies. This means that the atomic energy must be subtracted from the band energy E_{bs} which removes all sensitivity to s_0.

The rms error for the final silicon calculations ranged from 0.33 eV for the low volume (75% of the tetrahedral equilibrium volume) to 0.12 eV for the large volume (190%). For the volumes in between, the error dropped through this range. The sum of errors stayed consistently around 0.5–1.0 eV for the 40 eigenvalues used to evaluate the band energy E_{bs}. Germanium fitting behavior differed little from silicon and the errors are much the same. This represented a very good fitting especially for five parameters as can be compared to similar errors for other works[4–6] with more free parameters; the residual error will be corrected in the repulsive term.

For the four interaction parameters, three were found to have very similar distance dependences for silicon. These three are $ss\sigma$, $pp\sigma$, and $pp\pi$, the parameters which do not mix s and p shells. This result is similar to the finding of Harrison for his universal parameters.[8] Even though these three had similar distance dependences, an attempt to try to make all four of the orbital parameters have the same distance dependence significantly increased the error in the fitting so that different distance dependences had to be allowed.

The distance dependence for the parameters differed significantly from the $\frac{1}{d^2}$ formulation. The overall values for the orbital parameters in silicon and their distance dependence are compared to $\frac{1}{d^2}$ in Fig. 1. It is similar for germanium. The new parameters drop much faster than had been assumed by previous works and are somewhat similar to the results obtained from one high-pressure state.[12,13] The sets of values were fitted to a distance dependence function. For the best fit, the dependence had the following form:

$$P = \frac{\alpha r^{-\beta}}{1 + e^{\mu(r - r_0)}},$$

where P denotes the parameter. Table I lists the values for α, β, r_0, and μ. As the NN distances grew, the values for all of the parameters except $sp\sigma$ began to drop faster than $r^{-\beta}$, requiring the addition of the Fermi function cutoff.

The power in the exponential μ for silicon is about twice that for germanium, while the distance r_0 for silicon is 0.23 Å smaller than germanium's value. If the CA exchange-correlation is also used for germanium, r_0 for silicon is nearly the same as it is for germanium, showing the difference that the correlation can make in the band structure. The actual value for μ varied some from one parameter to another, but for simplicity it was set to one single value as much as possible. This same idea applies to the r_0 value which for silicon is about 3.35 Å and for germanium about 3.58 Å. The $sp\sigma$ parameter still maintains its uniqueness by having a μ equal to zero in each set.

An attempt was made to force these parameters to follow a $\frac{1}{d^2}$ formula in the fitting, but this worked only with large errors. At one point second nearest neighbors were allowed and this produced better results, but at about 120% volume, the second nearest neighbors are at the distance of the third nearest neighbors (about 4.05 Å) for the 75% volume. A good fit for both 120% and 75% could not be found in third NN calculations when the 4.05 Å value of one was used for the other volume or vice versa. Trying to force the second NN values to zero before 120% volume did not work due in part to $sp\sigma$'s dropping off slowly in the second-nearest-neighbor range. This meant that each "rank" of neighbors would need its own set of parameters, more than was wanted for simplicity.

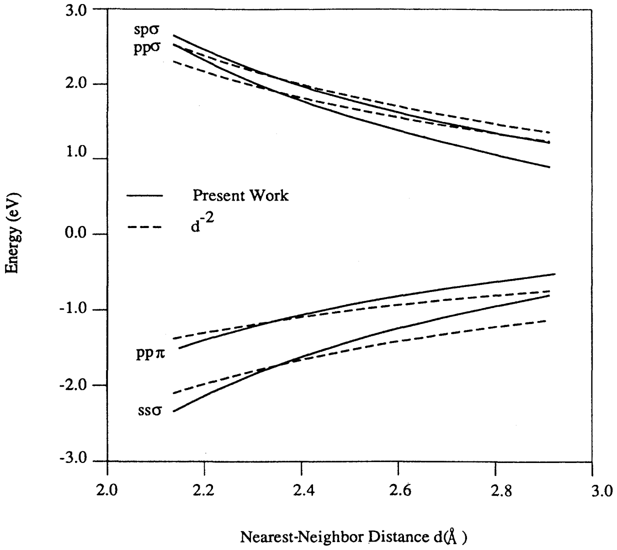

FIG. 1. Distance dependences of the tight-binding parameters for silicon. Comparison with the standard $\frac{1}{d^2}$ dependence is shown. The parameter values for the $\frac{1}{d^2}$ curves were made to coincide with the present values at the zero-pressure nearest-neighbor distance (2.35 Å).

The actual band structures for silicon and germanium are shown in Figs. 2 and 3. Overall the valence-band fit is excellent. There are a few points that showed some problems. One is the flatness in the W-X direction (Z direction); this has been attributed to the use of first NN parameters.[27] In addition, along the Σ direction particularly near Γ, the top valence band seems to be flatter

TABLE I. Tight-binding parameters of silicon and germanium obtained from fitting to the band structure of *ab initio* calculations.

	α (eV)	β	r_0 (Å)	μ (Å^{-1})
		Silicon		
$ss\sigma$	−24.0595	3.06275	3.35	4.5
$sp\sigma$	35.4233	2.50265	3.35	0.0
$pp\sigma$	23.7901	2.94507	3.35	4.5
$pp\pi$	−14.8426	2.99327	3.35	4.5
		Germanium		
$ss\sigma$	−34.3736	3.27888	3.58	2.0
$sp\sigma$	54.3302	2.86020	3.58	0.0
$pp\sigma$	29.9416	2.95436	3.58	2.0
$pp\pi$	−14.4741	2.86134	3.58	2.0

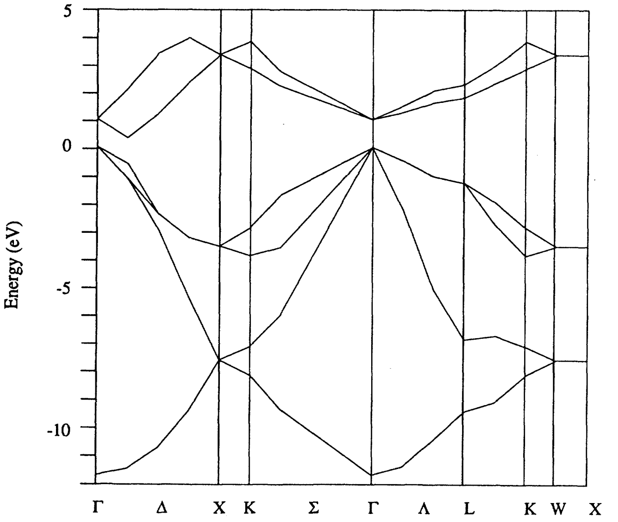

FIG. 2. The valence part of the silicon band structure (at zero pressure) obtained from the present tight-binding parameters for Si.

than the *ab initio* bands. This is probably due to the particular parameters chosen since they were seen to change this behavior. It could also be an artifact of first NN parameters. The conduction band is only approximately fitted producing its worst behavior around X and Γ. At X the conduction bands are too high, while at Γ they are too low. The Γ values changed with different parameters, but it has been known[5,28] that more orbitals (first NN or otherwise) are needed to obtain reasonable conduction-band results.

It is interesting to note which orbitals have the strongest and weakest distance dependence. For every fit, the $ss\sigma$ parameter had the strongest dependence on distance. This is somewhat unusual since these orbitals are nondirectional and could be assumed to have a free-electron-type behavior which would lead to a $\frac{1}{d^2}$ dependence. Yet the weakest distance dependence occurs for the $sp\sigma$ interactions, while the pp interactions are similar to $ss\sigma$ for silicon and $sp\sigma$ for germanium.

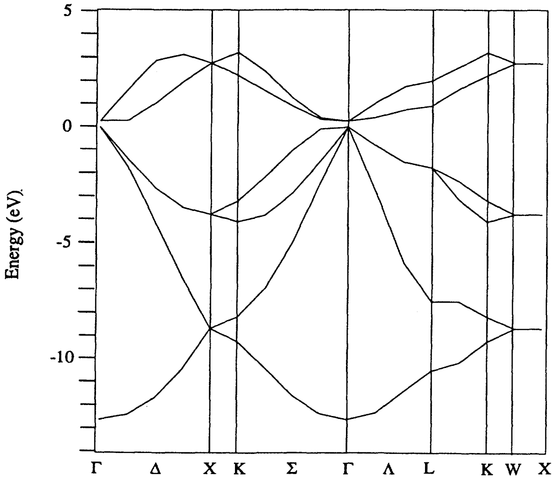

FIG. 3. The valence band of germanium obtained from the present tight-binding parameters.

A possible explanation exists in the extent of neighbor interactions in *ab initio* calculations which in principle include all of the neighbors. Therefore, the changes that occur in the *ab initio* calculations with more distant neighbors would have to be included in the NN tight-binding parameters; this could lead to differently varying behavior among some of the parameters. The fact that in the germanium results the variations of two or three orbitals are much weaker compared to $ss\sigma$ than they were for silicon might support this since germanium can be thought of as more metallic and therefore more dependent on distant neighbors. However, $ss\sigma$ for germanium is more strongly dependent on distance than it was for silicon. It seems unlikely that any concrete conclusions can be drawn about the specific origins of the varying distance dependences.

III. REPULSIVE POTENTIAL AND TOTAL ENERGY

To calculate the total energy, extra terms representing the ion-ion interaction and a correction for the over counting of the electron-electron interaction will need to be added to the band energy. The form for these corrections is usually repulsive and can be quite simple or very complicated depending on the need for accuracy and flexibility. The repulsive fitting provided for many more options than the fitting of the E_{bs} sum did. Forms using distance only, bond number, angles, and charge transfer have been presented by others.[11,17–20] Many of the forms give very good results for only a few structures or give limited results for a larger set of structures. Of interest here was obtaining a formulation that covers a much wider group of structures with a very high degree of accuracy.

The E_{bs} was provided by the new parameters for each structure that was included in the fitting. In order to insure that the E_{bs} values were accurate 216 k points in the Brillouin zone were used to obtain the band-structure energy for all crystals except for the tetrahedral form. This number of k points showed convergence to about 0.04 eV for the body-centered-cubic (bcc) structure and to less than 0.04 eV for the simple cubic (sc) and face-centered-cubic (fcc) structures.

To do the fitting a data base of total energies for the tetrahedral, β tin, sc, bcc, and fcc was needed. Tetrahedral energies came from the same LDA calculations where the electronic eigenvalues were obtained. The other energies were taken from plots made by Yin and Cohen[26] for β tin, sc, bcc, and fcc. In addition, energy curves of silicon dimer and trimer were taken from earlier calculations.[18,29] Si_2 had a minimal contribution to the fitting; the repulsive potential needed for a good fit was found to be about 15% greater than the tetrahedral repulsion. Similarly, the Si_3 repulsion was found to be about 7% greater than the tetrahedral repulsion. These approximate repulsive strengths were the only data from the clusters that were included in the fitting. This resulted in 60 fitting points across the five structures for silicon (with some idea of how Si_2 and Si_3 differed from the crystals) and in 54 points in five structures for germanium (the trend found for silicon clusters was used in germanium). Once the total energy and the E_{bs} are known the repulsive potential can easily be found for each structure. A least-squares fitting routine was then used to find a formulation for the repulsive energies.

For silicon the repulsive values divided by the number of nearest neighbors are shown in Fig. 4. It can be seen that the repulsive strength drops off as a function of distance and of structure (increasing coordination). The axial ratio for β tin has, except in the test cases, been set to 0.5516 for silicon and 0.5512 for germanium.[30] This gives four nearest neighbors plus two more 6% further away. Typically this has been taken to mean that β tin has six nearest neighbors, suggesting that the only difference from sc is a distance change for two nearest neighbors and bond angle changes. To check this the number of nearest neighbors for β tin was determined by observing the changes in the E_{bs} when the contribution of symmetric pairs of atoms were removed from the β tin structure. If the pairs all have the same contribution, then they should produce similar results when removed compared to the unaltered structure. The E_{bs} did not indicate this. Instead it showed that the removal of two of the four nearer-neighbor contributions produced nearly twice the effect as the removal of the two more distant neighbors did. Therefore, β tin was assumed to have the equivalent of more than five but less than six nearest neighbors (5.5 were assumed) of roughly equal distance for this particular plot and axial ratio.

By considering only the regions of interest around the minimums of each structure a similarity to the tetrahedral repulsion per neighbor might be seen. When the values shown in Fig. 4 are divided through by the tetrahedral repulsive energy per neighbor, nearly flat and straight lines result. By connecting the lines at the minimum energy nearest-neighbor distance, an S-shaped line appears. Each repulsive curve shown can be described by a constant times the tetrahedral repulsive energies. The values for these constants in silicon versus nearest-neighbor distance are shown in Fig. 5. The equilibrium nearest neighbor distance for each structure is marked in the figure. Superimposed on the lines is a curve that goes through the equilibrium NN distance. The lines shown are actually the structure-dependent terms used in the final fitting for silicon as shown in Fig. 6. From this, it can be seen that a two-body interaction alone is not sufficient to describe the binding, but that a simple structure-dependent constant combined with the tetrahedral two body potential would be more appropriate. This constant fell off in silicon from the tetrahedral value of one to about 0.97 for β tin to 0.92, 0.80 and 0.76 for sc, bcc, and fcc, respectively. For Si_2 there was a noticeable difference in curvature between the true curve and the curve given by a percentage of the tetrahedral two body. This difference can probably be associated with the fact that in Si_2 multiple bonding takes place which would strengthen the bond but also give it a much stronger distance dependence than that of a single bond system. For Si_3 the curvature difference was also present, although it was much less noticeable.

For germanium, the results are all very similar, as can be seen in Fig. 7. The lines shown are the structure-dependent terms used in the final fitting for Ge as shown in Fig. 8. The S-shaped curve for germanium is not as steeply descending as the one for silicon (Fig. 5) was. This might be due to a number of things, including the more metallic nature of germanium and the fitting-

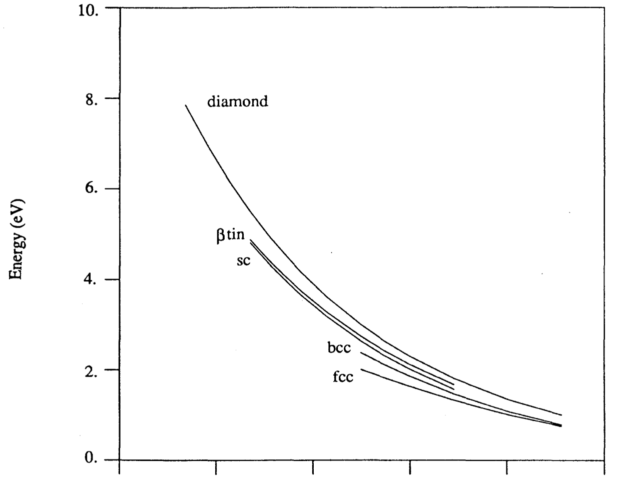

FIG. 4. Silicon repulsive energies per nearest neighbor calculated as the difference of the *ab initio* binding energy and the tight-binding E_{bs} divided by the number of nearest neighbors. As discussed in the text, the number of nearest neighbors for β tin is taken as 5.5.

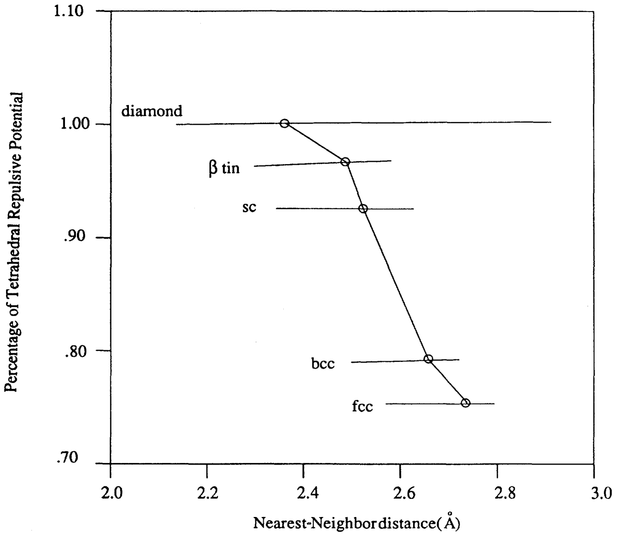

FIG. 5. Ratio of the repulsive energies shown in Fig. 4 with the diamond structure as the reference.

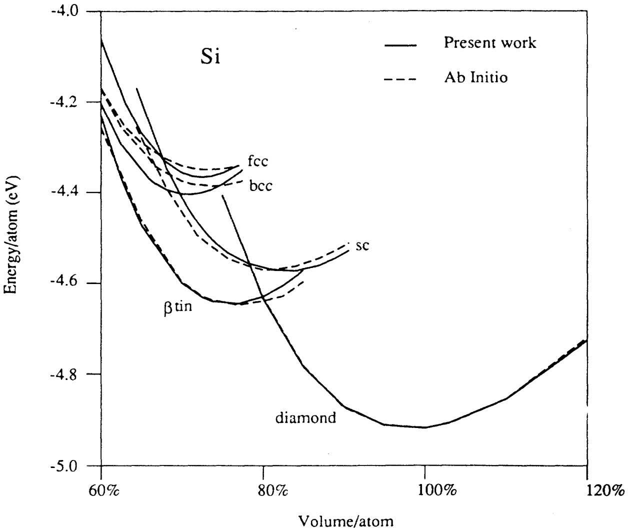

FIG. 6. Comparison of the total energies from the present model for silicon to the *ab initio* values fitted for.

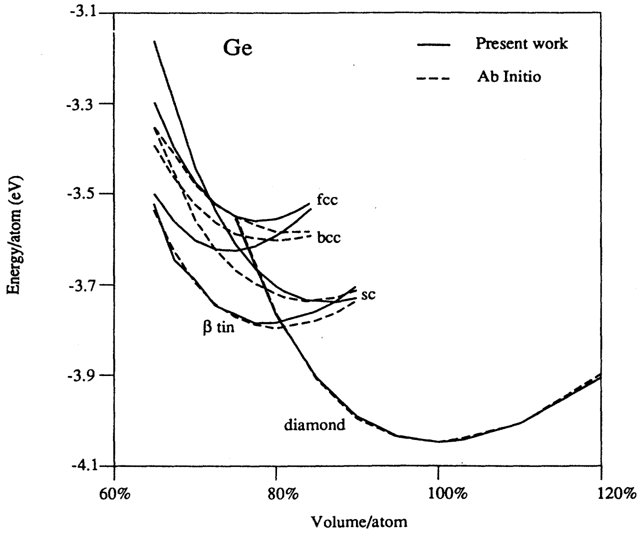

FIG. 8. Comparison of the total energies from the present model for germanium to the *ab initio* values fitted for.

dependent positioning of sc and bcc. The more metallic nature of germanium can be seen in the fact that the metallic phases and the tetrahedral phase have all moved closer to one another than they were in silicon. Certainly germanium has more distant bonds less localized and centered on the central atom than does silicon and this would seem to make the transition from the semiconducting state to the metallic state less pronounced.

The final form for the repulsive energy is

$$E_{\text{rep}} = \frac{1}{2}\sum_{\substack{i,j\\ i\neq j}} C_{ij}\omega_{ij} r_{ij}^{a_1} e^{-a_2 r_{ij}},$$

where ω is a symmetric function ($\omega_{ij} = \omega_{ji}$) which is dependent on the local environment. The pairwise interaction $r_{ij}^{a_1} e^{-a_2 r_{ij}}$ is determined by the diamond curve. The S-shaped function ω is given by

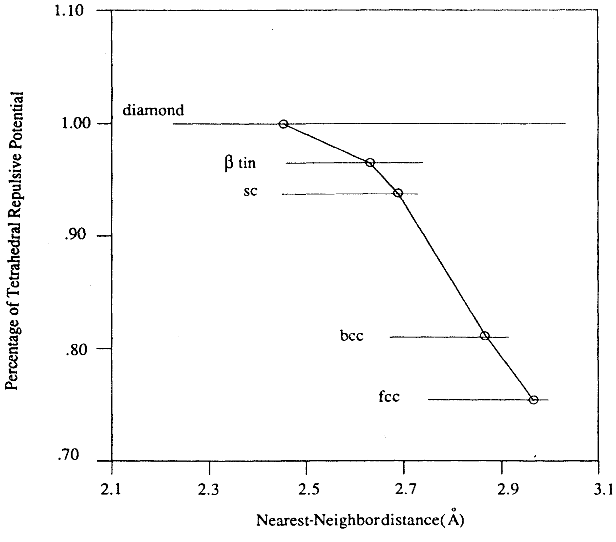

FIG. 7. Same as Fig. 5 for germanium.

$$\omega_{ij} = \frac{b_1}{1 - b_3 e^{-\xi_{ij} - b_3}} + \frac{b_2}{1 + e^{b_4 \xi_{ij} - b_5}}.$$

The structure-dependent variable ξ_{ij} is then based on a symmetrized sum involving bond angles over the nearest neighbors as

$$\xi_{ij} = 0.5\left(\sum_k \Gamma_{ijk}\Phi_{ijk} + \sum_k \Gamma_{jik}\Phi_{jik}\right)$$

with Φ_{ijk} given by

$$\Phi_{ijk} = \frac{1}{1 + b_3 e^{-b_6 \cos(\theta_{ijk} - \pi/6)}} + \frac{1}{1 + b_3 e^{-b_6 \cos(\theta_{ijk})}}.$$

The convention used for θ_{ijk} is that the central atom is i and the atom to be considered for bonding with i is j and that k are the other atoms in the system. The function Γ

$$\Gamma_{ijk} = \frac{1}{1 + \left(e^{c_1 (r_{ik}/r_{ij} - 1) - c_2}\right)^2}$$

serves to limit second-nearest neighbors in the summation over k. While the cutoff function C_{ij} prevents second NN contributions to E_{rep},

$$C_{ij} = \frac{1}{1 + e^{c_2 (\Gamma'_{ij} - c_3)}},$$

where Γ'_{ij} differs from Γ_{ijk} and is given by

$$\Gamma'_{ij} = \sum_k \frac{c_2}{1 + e^{c_1 (r_{ij}/r_{ik} - 1)}}.$$

The two-body potential for silicon is identically fitted to the tetrahedral structure so that ω is 1. All other forms were then fitted by adjusting the parameters in ω and ξ. The denominator in the first part of ω is for the lower coordinated structures where an increase in the repulsion per bond is needed. This part was not strictly fitted, but rather the general idea of ω being about 1.15 for Si_2 was kept in mind. The parameters are tabulated in Table II. In germanium, the original tetrahedral fit (0.0049 eV rms) was at least twice as good as the same fit for silicon (0.014 eV rms, shown in Fig. 6). Since the error bars for this calculation are on the order of 0.01 eV, the two-body term for germanium was fitted to both the tetrahedral and β tin form raising the error for tetrahedral germanium to 0.011 eV rms and it is this fitting that is shown in Fig. 8. The error in the other structures roughly increased with increasing coordination. Binding energy errors were determined by taking the difference between the *ab initio* and present calculations at the *ab initio* minimum volume. Minimum-energy error was found by taking the difference between the lowest energies for both *ab initio* and present work. By comparing the minimum-energy volume from *ab initio* and present work the volume errors were found. These errors are listed in Table III. For germanium, the errors were higher in the cubic structures than they were for silicon.

The comparison for silicon to the *ab initio* energies is quite good over all of the structures. The transition region of β tin and the diamond structure are virtually identical to the *ab initio* values. sc and fcc are also very well fitted, while bcc shows more noticeable error. The fitting actually went out to 190% of the diamond structure for all of the models, but is not shown in the figures in order to emphasize the higher coordinated structures. For germanium, the tetrahedral structure is very well fitted as is the β-tin structure particularly in the lower volume region from which it makes a transition to the diamond structure. The cubics for Ge presented something of a problem and, although reasonably well fitted, are not as accurate as the two lower energy structures.

TABLE II. The parameters of the repulsive potentials for silicon and germanium in the total energy expression.

Silicon	
$a_1=-1.772632$	$a_2=-1.904299$
$b_1=973.63688$ eV	$b_2=317.05143$ eV
$b_3=0.25$	$b_4=1.25$
$b_5=9.92$	$b_6=12$
$c_1=50.0$	$c_2=6$
$c_3=35$	
Germanium	
$a_1=0.704324$	$a_2=-2.975697$
$b_1=1940.6717$ eV	$b_2=648.2367$ eV
$b_3=0.355$	$b_4=1$
$b_5=8.15$	$b_6=12$
$c_1=50.0$	$c_2=6$
$c_3=33.3$	

The form of the potential is only a little more involved than many classical potentials for silicon (and germanium).[31–36] By stating that all formulas apply only to first-nearest neighbors, the cutoff functions could readily be removed, producing a much simplified version. Indeed, the number of parameters in the repulsive potential is similar to some classical potentials and in some cases are far fewer than other classical potentials.[37]

A note should be made about the total energy for the minimum energy structures. As seen in Fig. 6, the lowest energy for silicon is 4.92 eV/atom taken from the *ab initio* calculation which is well below the experimental value of 4.63 eV/atom.[26] The data for the higher coordinated structures came from calculations using the Wigner exchange correlation; the value for diamond silicon with this correlation is about 4.67 eV/atom.[26] It was necessary therefore to move the higher coordinated structures down by about 0.3 eV/atom so that they maintain their relation to the lower diamond value. This would mean that the silicon results should be moved up by about 0.3 eV/atom. However, since this shift originated out of the *ab initio* work and not with any of the fitting, it will not be made here. The shift will be kept in mind when other energies for test cases come out too low.

As intended the crystal structures all are fitted very well with this formulation. The main areas of interest are the structures which have coordinations similar to the minimum-energy structure. However, even outside of this tetrahedral region the fitting seems to provide the most accurate binding information available within the framework of orthogonal tight-binding models. In agreement with the work of others,[11,20] a simple two-body term is sufficient to give good tetrahedral repulsive energies. Perhaps the most interesting part of the repulsive fitting is that the other structures can be described well by a constant percentage of the tetrahedral repulsion. It has been suggested[31] that the change from the tetrahedral structure to the more metallic phases should be a discontinuous or first-order phase transition which would produce an S-shaped curve microscopically and this is what was found for the value of ω as the coordination increases. A simple interpretation of ω is that it serves as a shielding term as though the electrons were blocking the full repulsion of the ions as in a screening effect.

The range of extremely good fitting for silicon is much larger than that for germanium due most likely to the fact that the *d* orbitals should play a larger role in germanium and have not been included in the calculations. This becomes more important in sc and bcc which have regions of poorer fitting. For fcc, the E_{bs} and $E_{\rm rep}$ are sufficient to cover the lack of *d* orbitals to get a good minimum energy and volume but the curvature is far from perfect.

As mentioned, a total energy TB model[13] was developed for silicon using approximate pressure-dependent distance dependences.[12] Some aspects of that model are similar to the present work and the two give similar volume accuracies. By using distances to determine the coordination, the previous model[13] is simpler in form, although it goes out to different neighbor rankings for different structures. The structure dependence there and

TABLE III. Errors in the fitting for different crystal structures.

	Diamond	β tin	sc	bcc	fcc
	Binding energy error (eV)				
Silicon	0.014	0.015	0.030	0.030	0.041
Germanium	0.009	0.017	0.079	0.058	0.033
	Minimum energy error (eV)				
Silicon	0.001	0.006	0.002	0.018	0.016
Germanium	0.000	0.011	0.002	0.024	0.023
	Volume error				
Silicon	0	≈ 0	+4%	−5%	−1%
Germanium	0	−1%	+4%	−5%	−5%

here is a weighted count of the number of neighbors. The simpler structure dependent form, though, can cause problems. When this weighting is based solely on distance as in the previous model, the values can change quite a bit for β tin, depending on the axial ratio. However, the E_{bs} does not change at the same rate. In fact, when the axial ratio is about 0.516, then all of the first NN in β tin are at the same distance indicating a sixfold system which would give a repulsive strength per neighbor similar to sc. This sc repulsive strength for β tin is too weak to offset the E_{bs}. Certainly, if β tin were not important then the simpler form would be quite good. However, β tin is one of the few higher pressure forms for silicon that has actually been produced experimentally and accuracy regarding it would be well worth the slightly more complicated form presented. The present results for β tin and bcc volumes are better, and it is unlikely that there would be any structure problems with β tin. The sc and fcc volumes are slightly poorer, but are still extremely good.

Other works have attempted to use the Si_2 repulsive potential for all of the structures.[18,19] This was also attempted with the present TB model. The use of the Si_2 repulsive form for the crystals definitely produced far worse results than using the tetrahedral repulsion. This could, in general, be expected since Si_2 is a multiply bonded system not at all like the crystals. Using the tetrahedral repulsive potential then would be in question for Si_2, but as presented shortly the results were still quite good showing a better transferability from tetrahedral to other structures than from those structures back to tetrahedral.

IV. TEST CASES

It is certainly important to test the form for any potential that is produced so as to judge its validity in the systems that it may later be applied to study. Other forms tried were thrown out because of a large error in one or more of the test cases. Here a number of results will be given indicating the strengths and weaknesses of the present models.

A. Clusters

The energies and bond distances for silicon and germanium clusters are shown in Table IV along with *ab initio* and experimental values.[29,38–46] The fitting for the Si_2 molecule is quite good for the minimum-energy bond distance and gives an acceptable value for the energy minimum itself. When applied to Si_3, the minimum-energy bond distance of 2.15 Å is in excellent agreement with the *ab initio* value of 2.17 Å.[29] The minimum-energy central bond angle of 86° is found to agree well with the *ab initio* values. The bond angle represents a small error from the value that Jones[39] gives of 85° and a larger error for the value of Raghavachari at 77.8°.[29]

Germanium clusters produced very similar results. Ge_2 was found to have a bond distance of 2.50 Å, again in reasonable agreement with *ab initio* values[41,42] and

TABLE IV. Comparison of the cluster results with *ab initio* calculations and experiment.

	Present	*ab initio*	Expt.
	Cluster binding energies (eV)		
Si_2	3.7	4.3,[a] 2.6[b]	3.2[c]
Si_3	9.2	6.4,[b] 8.8[c]	7.7[d]
Ge_2	3.0	4.1,[e] 2.5[f]	2.8[g]
Ge_3	7.8	6.4[h]	6.5[i]
	Bond lengths (Å)		
Si_2	2.24	2.26,[a] 2.23[b]	2.24[c]
Si_3	2.15	2.17,[b] 2.27[c]	
Ge_2	2.50	2.34,[e] 2.43[f]	2.44[h]
Ge_3	2.27	2.29[j]	
	Angle (deg)		
Si_3	86	78,[b] 85[c]	
Ge_3	88	85[j]	

[a] Reference 38.
[b] Reference 29.
[c] Reference 39.
[d] Reference 40.
[e] Reference 41.
[f] Reference 42.
[g] Reference 43.
[h] Reference 44.
[i] Reference 45.
[j] Reference 46.

the energy is found to be −1.5 eV per atom. Ge_3 also has very good results for the bond angle and for the bond distance.[46] Thus, although the fitting did not include the cluster values in strict detail, the results are quite reasonable.

B. Phonons and defects

These models were tested also to see how well they reproduced some of the dynamic and defect properties. Wang, Chan, and Ho[20] found that using tight-binding techniques and a distance-dependent repulsive form was sufficient, at least with their values, to give good results for the phonon frequencies. They also checked shear constants and found low but, perhaps, reasonable results. The values for the phonon frequencies obtained with the present models are shown in Table V and can be compared to *ab initio* and experimental values.[47–49] Silicon is in good agreement with *ab initio* values, but the germanium values are noticeably high. No reasonable way of reducing the germanium values was found. Based on the results for silicon, the tight-binding method can produce good phonon results. The most likely reason for the germanium discrepancies lies with the fact that germanium has some small contributions from sources outside of the *s* and *p* orbitals and the first NN interaction.

The value for c_{11}-c_{12} for silicon is rather low. This apparently is a common behavior of tight-binding calculations that have produced good phonon results.[50] While the germanium values for the phonons were too high, the value for c_{11}-c_{12} is, on the other hand, too small. Certainly it might be reasonable to question tight-binding abilities to produce these values while maintaining accuracy elsewhere. The energy scale used to determine the phonons and shear is extremely small so that even a small difference could produce seemingly large errors. What is more interesting is what it might take to get good phonon values and shear constants for these structures since the distortion due to shearing to find c_{11}-c_{12} is somewhat similar to one of the phonon modes [LOA(X)].

TABLE V. Silicon and germanium phonon and shear values as compared to density-functional theory (DFT) (Refs. 47 and 48) and experiment (Ref. 49). Phonon values are in THz and shear value is in erg/cm^3.

	Present	DFT	Expt.
	Silicon		
LTO(Γ)	14.7	15.2	15.5
LOA(X)	11.2	12.2	12.3
TO(X)	14.4	13.5	13.9
TA(X)	4.5	4.45	4.49
c_{11}-c_{12}	5.02	9.8	
	Germanium		
LTO(Γ)	10.6	8.9	9.1
LOA(X)	10.6	7.1	7.2
TO(X)	12.1	7.8	8.3
TA(X)	4.3	2.4	2.4
c_{11}-c_{12}	4.23	8.5	

The defect energies for silicon are in excellent agreement with *ab initio* calculations. The vacancy has a value of 3.76 eV for formation, the T interstitial has a value of 4.95 eV, and the X interstitial has a value of 5.76 eV. The corresponding *ab initio* values are 3–4 eV for the vacancy, 5–6 eV for the T interstitial, and 4–6 eV for the X interstitial.[33,51] The defects were relaxed with Hellmann-Feynman forces.[15,20,52] The vacancy showed almost no movement, which disagrees with some recent calculations indicating an inward (toward the vacancy) relaxation.[53,54] A possible reason for the almost nonexistent relaxation might be due to the fact that the formulation is limited to nearest-neighbor distances, which would not allow interactions across the vacancy. It has been suggested that it would be better to allow more distant interactions.[1] To test this, a cutoff of 4.0 Å was used. In this calculation, the atoms around the vacancy moved toward the vacancy suggesting that more distant interactions would be useful for such calculations.

C. Bulk structures

Certain tests were also performed for bulk structures. One of the most important ones was the β-tin relaxation test that served to eliminate an otherwise good potential. The formulation that has been presented above was worked out so that this would not happen. Thus the β-tin relaxation is expected to be extremely small, indicating that it is very near equilibrium at the axial ratio given by *ab initio* calculations and experiment.[26,30]

Another test case is the BC8 structure for silicon.[55] This is a fourfold coordinated system in which the atoms have been rearranged from the tetrahedral form. With the present formulations the minimum energy is correct to approximately 0.015 eV per atom and that the minimum volume per atom is about 2.5% off of the *ab initio* values.[55] A final bulk test was conducted on BCT5, a new structure proposed for silicon in which the atoms are fivefold coordinated.[56] The equilibrium volume per atom came out to be about 7% in error while the two internal parameters agreed well with the *ab initio* values; however, the minimum energy came out to be slightly above sc when it should be roughly coenergetic with β tin.

Although the BCT5 structure may have large strain regions, which could lead to errors in the present model, the phonon and shear results would indicate that if this were the cause of the error it would produce too low of a value for the minimum energy. There is some possibility that the error in minimum energy could be due to the differences between the *ab initio* calculation used in the BCT5 work and the *ab initio* work used to generate the present model. This would allow the good agreement with the BC8 work since that *ab initio* calculation should differ little from the *ab initio* calculations used for the present work. However, this does not seem likely to explain the magnitude of the difference in energy and another suggestion seems appropriate. The formalism used here is strictly sp^3; certainly for the tetrahedral structure this is sufficient for most concerns. As the coordination increases other orbitals, specifically d, orbitals become more important.

While this model produces excellent results for silicon in all of the structures fitted, it is noticeable from the germanium calculations that there are some regions where sp^3 may represent a good approximation but does produce noticeable error. For silicon this region probably occurs around the BCT5 structure. Although it has only five nearest neighbors, they are oriented such that one neighbor is very close to the central atom while the other four are pressed more towards one another. This is not completely different from a surface situation and as has been found[16] some of the surface bonding is more strongly d orbital dependent.

V. CONCLUSION

We have performed a thorough tight-binding fitting to *ab initio* band structures for both silicon and germanium over a number of pressures. It is found that the distance dependence for the tight-binding parameters ranges from $r^{-2.5}$ to $r^{-3.3}$. This differs significantly from the previously assumed $\frac{1}{d^2}$ behavior. Total energy models based on the tight-binding work and on an S-shaped function multiplied by the tetrahedral pairwise repulsive potential produce very good fittings over a number of structures. Furthermore, test cases show reasonably good agreement with bulk and cluster properties, indicating the high transferability of the models.

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