

New empirical approach for the structure and energy of covalent systems

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Empirical interatomic potentials permit the calculation of structural properties and energetics of complex systems. A new approach for constructing such potentials, by explicitly incorporating the dependence of bond order on local environment, permits an improved description of covalent materials. In particular, a new potential for silicon is presented, along with results of extensive tests which suggest that this potential provides a rather realistic description of silicon. The limitations of the potential are discussed in detail.

I. INTRODUCTION

Recently there has been intense interest in developing simple model interatomic potentials, which would permit direct calculation of the structural properties and energetics of complex systems, in particular semiconductors.¹⁻⁶ Pair potentials have long been used to describe rare-gas atoms, simple metals, and highly ionic systems. However, such interesting materials as semiconductors, ceramics, polymers, and refractory metals all exhibit covalent bonding, which creates serious problems for traditional empirical approaches.

This paper describes in detail a new approach to the formulation of interatomic potentials for covalent systems. A brief description of the early stages of this work was given elsewhere.⁴ The central idea is that, in real systems, the bond order (i.e., the strength of each bond) depends upon the local environment.⁷ In particular, an atom with many neighbors forms weaker bonds than an atom with few neighbors. For more covalent materials, this dependence is sufficient to stabilize structures with low atomic coordination number (number of neighbors). Including this dependence explicitly appears to solve some of the most serious problems of describing covalent systems without introducing any major increase in computational complexity.

As an application of this general approach, a new empirical potential for silicon is developed. Silicon represents a particular challenge because it has many polymorphs with qualitatively different bonding which, nevertheless, have perversely similar cohesive energies. The potential developed here is noteworthy in being able to describe the polymorphous perversity of silicon. This potential represents a considerable improvement over that reported earlier.⁴ In particular, despite its limitations, the present potential appears to be sufficiently "global" to be used in molecular-dynamics simulations.

This paper first reviews some relevant previous work in Sec. II. Section III describes the new approach developed here, emphasizing its general properties and distinguishing features. An artificially simplified model for silicon is developed and analyzed in Sec. IV, illustrating the important features of this approach. Section V presents a more realistic potential for silicon, along with

results of extensive tests, which demonstrate the accuracy of this model while identifying its most important remaining weaknesses. Finally, Sec. VI summarizes the conclusions to be drawn from this work.

II. BACKGROUND OF THE PROBLEM

There are many problems in physics, chemistry, and materials science which require for their solution a knowledge of the total energy of a system of atoms as a function of the atomic coordinates. A few examples are determination of surface reconstructions, diffusion paths and barriers, reaction coordinates and barriers, phonon dispersions and interactions, and mechanical and thermal properties of materials.

In some cases, considerable progress has already been made using quantum-mechanical calculations.⁸⁻¹² However, for problems which involve large systems or which require statistical averages, quantum-mechanical calculations are at present not feasible because they are so numerically intensive. Despite recent progress in this respect,^{13,14} it is clear that there will always be interesting problems beyond the reach of *ab initio* approaches.

One solution to this problem is to construct an empirical interatomic potential $E(\{\mathbf{r}\})$, which gives the total energy E of a set of particles, as an explicit mathematical function of the set $\{\mathbf{r}\}$ of particle coordinates. If this function is sufficiently easy to calculate, and if it gives a sufficiently accurate description of the real physical system of interest, then one can perform realistic calculations of the properties of quite large systems, or even of statistical ensembles of such systems. Of course, such an approach will inevitably involve a significant loss of accuracy, compared with *ab initio* calculations.

Until recently, most empirical interatomic potentials fell into two simple groups. One group consists of pair potentials, most notably the Lennard-Jones "6-12" potential and the exponential Morse potential. Such potentials can be directly applied to a completely arbitrary configuration of atoms but do not accurately describe any but the simplest closed-shell systems. In particular, pair potentials are completely inapplicable to strongly covalent systems such as semiconductors.

The other group of potentials are constructed to accu-

rately describe small distortions from the ground state in more complex systems such as diamond-structure semiconductors.¹⁵ Perhaps the most famous of these is the Keating model.¹⁶ Such potentials are useful for describing phonons and elastic deformations, but they cannot describe the energy of states which differ qualitatively from the tetrahedral ground state.

It is interesting to note that both these approaches correspond to the leading term in a mathematical expansion of the energy, viewed as a function of the atomic positions. The Keating model, and related approaches, are roughly analogous to Taylor expansions of the energy about its minimum. They can give rather accurate descriptions of small displacements, but they become progressively less accurate for large displacements. A recent review of such approaches has been given by Kane.¹⁵ The pair potentials, on the other hand, take advantage of a somewhat different expansion. The energy of N interacting particles may be written as

$$E = \sum_i V_i(\mathbf{r}_i) + \sum_{i < j} V_2(\mathbf{r}_i, \mathbf{r}_j) + \sum_{i < j < k} V_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + \dots, \quad (1)$$

where \mathbf{r}_n is the position of the n th particle and the function V_m is called an " m -body potential." The first (one-body) term corresponds to an external potential.

The first term which describes interactions of the particles is the second (two-body) term, which when taken alone constitutes a pair potential. Thus, in this expansion, the pair potential is the simplest possible model for the interaction of a set of particles. A general feature of physically reasonable atomic pair potentials is that they favor the formation of close-packed structures, so they are unsuitable for describing covalent systems, which assume more open structures.

For describing covalent systems, a natural first step was to include the next term in the expansion (1), i.e., a three-body potential. This additional term could stabilize more open structures, e.g., by favoring bond angles corresponding to those of the diamond structure. Recently Stillinger and Weber¹ proposed such an empirical interatomic potential, incorporating two- and three-body interactions, and used it in molecular-dynamics simulations of molten silicon. Another such empirical three-body potential was proposed by Pearson *et al.*²

Both of these potentials were designed to describe a relatively limited set of properties of silicon. While they made an important contribution in opening up a new approach, and have already found applications, it is too soon to tell what range of properties these potentials will prove useful for describing. In particular, Biswas and Harmann³ have criticized these potentials, noting that they do not describe even qualitatively the behavior of nontetrahedral polytypes of silicon.

Biswas and Hamann³ introduced a more ambitious agenda, which in fact provided the original motivation for the present work. They pointed out that the cohesive energies of many real and hypothetical arrangements of silicon atoms are known from reliable quantum-mechanical calculations. Examples include polytypes⁸

(especially high-pressure phases), surfaces,⁹⁻¹¹ and point defects.¹² One may therefore use this database as a starting point, and try to systematically construct an interatomic potential which will correctly reproduce the cohesion over a wide range of coordination and bonding topology.

Those authors therefore chose a relatively general parametrized form for their three-body potential, and fitted the parameters to reproduce their database of cohesive energies, primarily of bulk polytypes.⁸ Initial results were promising.³ However, after further very detailed investigations,¹⁷ those authors concluded that they are unable, with a three-body potential, to describe the energetics of all the diverse bonding geometries which they initially considered. Instead, by focusing on the most critical set of bonding geometries (e.g., point defects), they obtained a potential which should be useful in simulating many relevant properties of tetrahedrally coordinated silicon, but which to some extent retreats from the earlier goal of also describing polytypes accurately.

It is my suspicion that the inability of three-body potentials to describe a wide range of bonding geometries is a rather general result, and not merely a shortcoming of the specific forms assumed in previous work. As an alternative, a new approach was introduced⁴ going beyond the three-body potential.

The specific form which was first proposed⁴ for this model potential had some serious shortcomings. Phonon energies were quite high, and more important, the diamond structure was not the ground state of the potential. The potential was thus not suitable for molecular-dynamics simulations. An improved potential, based on the same ideas, is therefore developed here. Section III introduces the central ideas behind the present approach to formulating an empirical potential.

III. A NEW APPROACH

A. Role of bond order

The work of Biswas and Hamann¹⁷ suggests that a three-body potential is not adequate for accurately describing the cohesive energy of silicon over a wide range of bonding geometry and coordination. However, a general form for a four- or five-body potential would probably prove intractable, and would contain far too many free parameters.

In attempting to construct an accurate and tractable potential, it therefore seems natural to abandon the use of a general N -body form. Instead, the present approach attempts to identify the relevant physics and to build it directly into the form of the potential. Before focusing on silicon, it is useful to consider trends in the bonding of elements in a more general way.

From simple quantum-mechanical arguments,⁷ the more neighbors an atom has, the weaker the bond to each neighbor will be. The bond strength, or bond order, in general depends in a complicated way on the geometry; for example, even-membered rings might be favored over odd. However, as discussed further in Secs. IV and V, the most important single variable appears to be the coor-

dination number, i.e., the number of neighbors close enough to form bonds. The discussion here therefore focuses on coordination.

If the energy per bond decreases sufficiently rapidly with increasing coordination, then the diatomic molecule will be the most stable arrangement of atoms. (The additional weak cohesion of molecular solids due to long-ranged intermolecular forces is not of interest here.) Such low coordination is the rule for atoms at the far right of the Periodic Table, especially near the top. Fluorine, at the top right corner, is the extreme case.

On the other hand, if the bond order depends only weakly on coordination, then one expects close-packed structures to form, in order to maximize the number of bonds. This extreme corresponds, roughly speaking, to metallic rather than covalent bonding. Such behavior is found for atoms at the left and bottom of the Periodic Table. In between, there is a systematic trend from low coordination at the upper right to high coordination at the lower left.

This trend suggests a picture in which the bond order is a monotonically decreasing function of coordination, with the trade off between bond-order and number of bonds determining the equilibrium coordination. In most cases one effect or the other dominates the trade-off. Only a small region of the Periodic Table provides the delicate balance necessary to yield intermediate coordination.

Silicon in particular is notable for the fact that, with modest changes of pressure, it can assume structures with a large range of coordination. The differences in cohesive energy among these structures are remarkably small.⁸ As discussed in Sec. IV A, this is because the decrease in bond strength with increasing coordination number very nearly cancels the increase in the number of bonds, over a large range of coordination. Silicon thus provides a particularly stringent test of our ability to accurately describe the dependence of bonding upon coordination, and therefore the dependence of cohesion upon structure.

B. Explicit form for the potential

Because of the crucial role of bond order and its dependence upon local geometry, it seems attractive to include an environment-dependent bond order explicitly into the potential in the following way. The interatomic potential is taken to have the form

$$E = \sum_i E_i = \frac{1}{2} \sum_{i \neq j} V_{ij}, \quad (2)$$

$$V_{ij} = f_C(r_{ij}) [a_{ij} f_R(r_{ij}) + b_{ij} f_A(r_{ij})].$$

Here E is the total energy of the system, which is decomposed for convenience into a site energy E_i and a bond energy V_{ij} . The indices i and j run over the atoms of the system, and r_{ij} is the distance from atom i to atom j .

The function f_R represents a repulsive pair potential, which includes the orthogonalization energy when atomic wave functions overlap, and f_A represents an attractive pair potential associated with bonding. The extra term f_C is merely a smooth cutoff function, to limit the range of the potential, since for many applications short-

ranged functions permit a tremendous reduction in computational effort.

The function b_{ij} is the sole novel feature of the potential. It represents a measure of the bond order, and is for now assumed to be a monotonically decreasing function of the coordination of atoms i and j . Determining a satisfactory form for b_{ij} is by far the most difficult part of applying this approach. In addition, terms which act to limit the range of interaction to the first neighbor shell are included in b_{ij} and are discussed in the following. The function a_{ij} consists solely of such range-limiting terms.

The form (2), which is based on physical and chemical intuition, already represents an extreme simplification from the most general mathematical form. For example, although (2) includes implicitly a three-body interaction, it might prove worthwhile in the future to include an additional term, with an explicit three-body form.¹⁸ Also, for some purposes it might be desirable to add a weak, long-ranged pair potential, e.g., in treating molecular solids or graphite.

The functions f_R , f_A , f_C , a_{ij} , and especially b_{ij} still need to be determined. As discussed elsewhere,^{4,7} the choice of exponential functions for f_R and f_A , as in a Morse potential, has the very desirable feature of leading automatically to the "universal" bonding behavior discussed by Ferrante, Smith, and Rose.¹⁹ This provides a compelling reason to take

$$\begin{aligned} f_R(r) &= A \exp(-\lambda_1 r), \\ f_A(r) &= -B \exp(-\lambda_2 r). \end{aligned} \quad (3)$$

The interested reader is referred elsewhere^{4,7} for further discussion of this choice.

Here the cutoff function is simply taken as

$$f_C(r) = \begin{cases} 1, & r < R - D \\ \frac{1}{2} - \frac{1}{2} \sin \left[\frac{\pi}{2} (r - R) / D \right], & R - D < r < R + D \\ 0, & r > R + D, \end{cases} \quad (4)$$

which has continuous value and derivative for all r , and goes from 1 to 0 in a small range around R . R is chosen to include only the first-neighbor shell for most structures of interest. The short range of the potential is numerically advantageous in many applications, and is important for the applicability of the simple ideas about coordination discussed here.

In the present work, b_{ij} is taken to have the following form:

$$\begin{aligned} b_{ij} &= (1 + \beta^n \zeta_{ij}^n)^{-1/2n}, \\ \zeta_{ij} &= \sum_{k \neq i, j} f_C(r_{ik}) g(\theta_{ijk}) \exp[\lambda_3^3 (r_{ij} - r_{ik})^3], \\ g(\theta) &= 1 + c^2/d^2 - c^2/[d^2 + (h - \cos\theta)^2], \end{aligned} \quad (5a)$$

where θ_{ijk} is the bond angle between bonds ij and ik . While $b_{ij} \neq b_{ji}$, this fact has no significance other than for

the (somewhat arbitrary) division of total energy into a sum of site energies in (2). If, for aesthetic reasons, a more symmetric form is desired, the sum over pairs of atoms in (2) can be replaced with a sum over bonds ($i > j$), and then b_{ij} can be replaced with the symmetrized function $\bar{b}_{ij} = (b_{ij} + b_{ji})/2$.

The form proposed for a_{ij} is

$$a_{ij} = (1 + \alpha^n \eta_{ij}^n)^{-1/2n} \quad (5b)$$

$$\eta_{ij} = \sum_{k \neq i, j} f_C(r_{ik}) \exp[\lambda_3^3 (r_{ij} - r_{ik})^3],$$

with α taken sufficiently small that $a_{ij} \approx 1$ unless η_{ij} is exponentially large, which will only occur for atoms outside the first-neighbor shell. However, in most of the present work, the cutoff a_{ij} is not actually used, i.e., $\alpha = 0$, so $a_{ij} = 1$. Equation (5b) is included for completeness, because the potential can probably be further improved with such a term.

In a previous publication,⁴ a different specific form for b_{ij} was assumed, which, rewritten to conform to the present notation, was

$$b_{ij} = \exp(-\zeta_{ij}/a),$$

$$\zeta_{ij} = \sum_{k \neq i, j} [f_C(r_{ik})/f_C(r_{ij})]^n \exp[n\lambda_2(r_{ij} - r_{ik})] g(\theta_{ijk}), \quad (6)$$

$$g(\theta) = [c + \exp(-d \cos \theta_{ijk})]^{-1}.$$

Initial results were encouraging, and several surface properties were described better than with (5). Unfortunately, for apparently reasonable parameters, (6) yielded a formation energy of essentially zero for the hexagonal-site interstitial. The existence of a zero-energy defect in the diamond structure indicates that the diamond structure is not the ground state for that potential. Therefore that potential could not be used for molecular-dynamics simulations, restricting its usefulness. Moreover, Dodson⁶ has argued that this reflects a general problem with the form (6), and does not just result from the choice of parameters.

While the present work was in progress, Dodson independently proposed⁶ a minor modification of (6) which appears to correct the most serious shortcoming, making diamond the ground state. However, that modified potential has not yet been extensively tested. Presumably it retains the rather high phonon energies of (6).

Before discussing the more successful form (5) for the potential, it is worthwhile to describe a highly simplified potential, which gives considerable insight into the important physical features which an empirical potential of the form (2) should embody. This simplified potential is the subject of Sec. IV and provides the starting point for the more accurate potential (5), which is discussed in Sec. V.

IV. MOTIVATING THE FORM OF THE POTENTIAL

A. A simple illustrative example

This section examines earlier quantum-mechanical results for silicon structural energies, and uses them to

motivate an exceedingly simple form for b_{ij} . That form, while inadequate for many applications, demonstrates how easily the overall behavior of silicon may be captured in an empirical potential of the form (2).

Figure 1 shows the cohesive energy per atom and per bond of silicon, for a number of high-symmetry structures, based on the results of self-consistent pseudopotential calculations within the local-density approximation (LDA) by Yin and Cohen.⁸ In the spirit of Sec. III A, we assume that it is justified to draw a smooth curve through these data, at least for the purpose of making qualitative arguments.

First, note that in Fig. 1 the energy per bond is a monotonically decreasing function of coordination, consistent with the ideas previously discussed. Second, note that over the range of coordination from threefold to twelfefold, the energy remains relatively constant. It is easily shown that, for a Morse potential of the form (3), with $\lambda_1 = 2\lambda_2$, and including only nearest neighbors, the cohesive energy per atom is independent of coordination when the bond-order parameter b_{ij} is proportional to $z^{-1/2}$, where z is the coordination number. Thus, to explain the relatively weak dependence of cohesive energy on coordination in silicon for $z \geq 3$, it is natural to assume that $b_{ij} \propto z^{-1/2}$ in the limit of large z .

To yield an energy minimum at an intermediate coordination, b_{ij} must at first grow more rapidly than $z^{-1/2}$ with decreasing coordination, but then it must saturate at low coordination. These two constraints are conveniently accommodated by assuming a potential of the form

$$b_{ij} = (1 + a^n \zeta_{ij}^n)^{-1/2n}, \quad (7)$$

$$\zeta_{ij} = \sum_{k \neq i, j} f_C(r_{ik}).$$

Here ζ_{ij} counts the number of other bonds to atom i besides the ij bond. When only the first shell of neighbors falls within the cutoff, $\zeta_{ij} \rightarrow z - 1$.

Equations (2)–(4) and (7) together constitute a complete form for a model potential. The simplifications in (7) are, first, the neglect of bond angles, and second, the

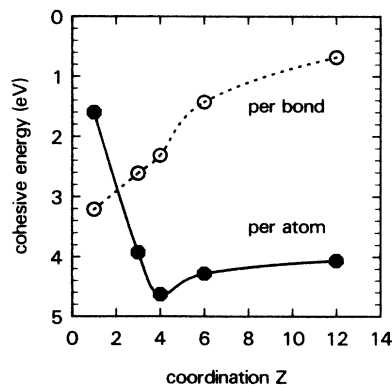


FIG. 1. Cohesive energy vs coordination number for high-symmetry structures: dimer molecule, graphitic, diamond, simple cubic, face centered cubic. Solid circles, energy per atom; open circles, energy per bond. Lines are spline fits to guide the eye. Cohesive energies taken from Yin and Cohen (Ref. 8).

neglect of distance (except via f_C) in defining the effective coordination ζ_{ij} . These effects are included in the more detailed form (5) of b_{ij} , which is discussed in the following section.

It is worth calling attention at the outset to the obvious pathologies of this simplified potential. All structures with, e.g., four nearest neighbors at equal distances have the same energy for this potential, so silicon is entirely stable in a two-dimensional square lattice. The shear modulus of the diamond lattice is identically zero, because of the lack of angular forces. If there are neighbors at distances comparable to the range of f_C , it becomes somewhat arbitrary whether they should be counted in ζ_{ij} , and so nonphysical values for b_{ij} and for the energy could result in such cases. Nevertheless, if we exclude obviously nonphysical structures, this almost trivial potential provides a remarkable description of the bonding properties of silicon.

Fixing $\lambda_1=2\lambda_2$ for simplicity, as in the traditional Morse potential, the five remaining parameters are chosen to fit the cohesive energy, lattice constant, and bulk modulus of diamond-structure silicon, and the calculated cohesive energy of the hypothetical graphitic and simple cubic phases. The resulting values are $\lambda_2=1.4654 \text{ \AA}^{-1}$, $A=2280.4 \text{ eV}$, $B=154.87 \text{ eV}$, $a=0.3685$, and $n=10.797$.

Since (7) gives a potential which depends only upon coordination (for structures where a single neighbor shell contributes), the results are conveniently summarized in Fig. 2, which is valid for any structure where all neighbors inside the cutoff are at equal distances.

Since this potential is only illustrative, the results will be sketched rather briefly. Bond lengths for the structures in Fig. 2 are described very well, except that the shortening for very low coordination is underestimated. [The accuracy is comparable to that of the potential (2)–(5) discussed in Sec. V B.] The energy of the zone-center optical phonon is correct to within 20%. The energy of the vacancy is found to be 2.9 eV, and of the tetrahedral-site and hexagonal-site interstitials, 4.5 and

2.6 eV, respectively. These defect energies are roughly consistent with results of LDA calculations,¹² to within the 1 eV accuracy typical of such calculations.

To show the importance of the choice of cutoff, the tetrahedral interstitial was recalculated with an abrupt cutoff at 2.5 Å, which excludes interaction with the six atoms at roughly 2.7 Å from the interstitial. This change drastically lowers the formation energy, from 4.5 eV to 1.1 eV. However, excluding the second neighbors is clearly unphysical in this case, since their distance is comparable to that of the first neighbors in a close-packed structure (e.g., 2.74 Å in fcc silicon).

For the Si(100) 2×1 surface,⁹ both the bond contraction of the dimers and the energy gain from dimerization are well described. For the hypothetical $\sqrt{3}\times\sqrt{3}$ Si adatom geometry¹¹ on Si(111), which is relevant to the Si(111) 7×7 , the geometries are well described for adatoms in both the “hollow” and “top” threefold sites, despite the quite large relaxations, and the nonintuitive fact that the top site is favored by about 0.6 eV is obtained correctly, albeit with a somewhat exaggerated gain of 0.9 eV.

Because of its surprising accuracy in a wide range of configurations, this simplified potential provides a good starting point for developing a more general potential. The form (5) used below was motivated largely by a desire to stay as close as possible to the form (7) while avoiding its pathologies.

B. Form of the potential

The results above provide convincing evidence that atomic coordination number is the main variable determining the bonding properties of silicon in different structures. Moreover, the form (7) seems to describe the dependence on coordination rather well. It is therefore convenient to keep the form (7) for b_{ij} , while altering the definition of the effective coordination ζ_{ij} in two ways. First, the relative distance of different neighbors should surely be taken into account in defining the effective coordination number. Second, some bond-angle term is needed to stabilize the diamond structure against shear, at least if the potential is to be kept short ranged.

Regarding the first point, we imagine that if atom i has two neighbors j and k , these atoms compete to form bonds with i . Both bonds are weakened, relative to the two-atom case. However, if the bond r_{ij} is much shorter (stronger) than the bond r_{ik} , it seems reasonable that the ij bond will not be appreciably weakened by the presence of the ik bond, whereas the ik bond will be drastically weakened.

Such an effect was already included in the earlier potential (6). However, the effect of small differences between the two bond lengths may have been exaggerated in (6), giving, for example, rather high phonon energies. In (5), therefore, ζ_{ij} is defined so that the effect is zero to first order in the difference between bond lengths, and only becomes large when the bonds differ by a length of order $1/\lambda_3$. One implication of this is that there is negligible bonding to atoms whose distance exceeds that of the nearest neighbor by more than a few lengths $1/\lambda_3$.

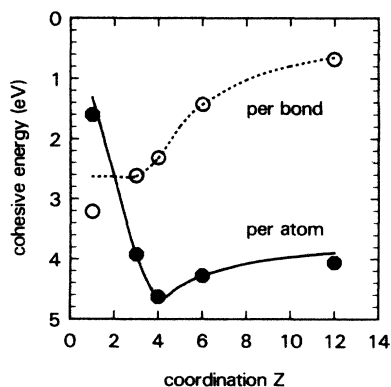


FIG. 2. Cohesive energy vs coordination number for the simplified model potential (7) of Sec. IV. Solid line, energy per atom; dotted line, energy per bond. Circles represent results of Yin and Cohen (Ref. 8) as in Fig. 1.

A similar cutoff on the repulsive interaction with relatively distant neighbors may be included, as in (5b). This is motivated primarily by a desire to minimize the effect of the (rather arbitrary) cutoff f_C in (2), while insuring that the interaction does not extend to the second-neighbor shell.

To introduce bond-angle forces into the potential, ξ_{ij} is modified in (5) so that other bonds ik to atom i weaken the bond ij more or less, depending on the angle between the two bonds. There is no reason, other than convenience, to restrict the dependence upon bond angle to the ξ_{ij} term, and it might be possible to further improve the potential by relaxing this restriction.

In (5), the parameter h is formally the cosine of the energetically optimal angle, although h is actually permitted to lie outside the range from -1 to 1 . The parameter d determines how sharp the dependence on angle is, and c determines the strength of the angular effect.

Unlike the earlier potential (6), the dependence on angle is no longer required to be monotonic. A prime motivation for this change was the desire to be able, in the future, to describe materials such as arsenic, which favor a bond-angle distribution which is not consistent with monotonic bond repulsion.

V. A NEW POTENTIAL FOR SILICON

A. Choice of parameters

The potential (2)–(5) is intended to be applicable to a wide range of elemental systems. Its usefulness in any particular application depends critically upon the choice of values for the parameters in the potential. Here I follow the approach introduced by Biswas and Hamann³ of systematically fitting the parameters to reproduce a database of known properties of silicon. It is worth stressing that, even for silicon, the uncertainties in the database (i.e., in calculated energies of silicon surfaces,^{9–11} defects,¹² and/or polytypes⁸) represent an important limitation here. For other materials, the dearth of data makes this procedure more problematic at present. Nevertheless, it is feasible for workers to generate their own data for the fitting procedure,³ so the application of this procedure is limited primarily by the considerable effort involved in generating an adequate database and fitting the parameters.

Applying this approach is unfortunately not straightforward, but rather requires a number of judicious choices based on physical intuition. This necessity arises because the potential will never be able to reproduce the entire database perfectly. One must therefore decide, first, what weighting to assign to the different data, i.e., what importance to assign to different atomic configurations. This choice depends in part upon what physical systems one intends to apply the potential to, e.g., small clusters where all atoms have low coordination, or high-pressure phase transitions where all atoms have high coordination.

In addition, one might choose to fit, not energies, but rather those differences in energies which are expected to be important. For example, it might not be worthwhile

to attempt to fit the cohesive energies of carbon in either the diamond or graphite structure to better than $1-2$ eV, but the difference in cohesive energies must be accurate to much better than 0.1 eV if one wants to obtain the correct ground state.

Because the energies of the configurations used in fitting the parameters must be calculated a very large number of times from the model potential, the database used here includes only very simple structures, mostly bulk polytypes, instead of making the fullest use of known energies of point defects, surface reconstructions, etc. The resulting values for the parameters are summarized in Table I.

Another factor in determining the parameters, which has been stressed by Dodson,⁶ is the desirability of performing a global search of parameter space to obtain the best fit to the database. Such a procedure was not attempted here, but it represents an attractive approach for future work. Unfortunately, techniques for performing global optimizations are inherently difficult, and Dodson implemented one such technique only with an exceedingly limited database. The use of a small database during the fitting is only justified if the resulting parameters are subsequently tested against a much larger database to verify their suitability, as was done here.

Finally, one serious limitation of the present study is that certain crucial parameters were not systematically optimized. Specifically, the two parameters R and D which define the cutoff function f_C were simply chosen so as to include the first-neighbor shell, but not the second, for several high-symmetry bulk structures. Some indications that this is not an optimal choice are described below. Also, the parameter λ_3 plays the role of a cutoff of sorts, and that parameter was simply taken equal to λ_2 because this seemed like a physically reasonable length scale. Results for $\lambda_3 = \lambda_1$ (which has no such physical rationalization) were also checked as a crude test. Similarly, investigation of the effects of including $\alpha \neq 0$ has barely begun.

While a more systematic determination of R , D , α , and λ_3 is both possible and desirable, there are some difficulties in this. In particular, these parameters become most significant in rather complex low-symmetry geometries, with neighbors distributed over a range of bond lengths. Thus the database used in the present study is probably not adequate to provide a physically meaningful determination of these parameters.

As a result of the several limitations previously discussed, the parameters presented here are certainly not the best set possible for describing silicon with the form

TABLE I. Suggested parameters for silicon, to be used in Eqs. (2)–(5). See text for discussion of expected accuracy of this potential, and for alternative values of R , D , α , and λ_3 .

$A = 3264.7$ eV	$B = 95.373$ eV	
$\lambda_1 = 3.2394$ Å ⁻¹	$\lambda_2 = 1.3258$ Å ⁻¹	
$\alpha = 0$	$\beta = 0.33675$	$n = 22.956$
$c = 4.8381$	$d = 2.0417$	$h = 0.0000$
$\lambda_3 = \lambda_2$	$R = 3.0$ Å	$D = 0.2$ Å

(2)–(5). Thus, the tests described in the following do not necessarily reflect fundamental limitations of (2)–(5). They may, in part, merely reflect the fact that an optimal set of parameter values has not been determined.

B. Tests and results

It is impossible, with a finite set of tests, to fully characterize such a potential, or to guarantee its success in any complex application such as a dynamical simulation. However, a serious attempt has been made here to test this potential more thoroughly than any other to date, at least insofar as is possible using static tests. The resulting catalog of achievements and shortcomings should be helpful in evaluating the appropriateness of this potential for any specific future application.

As a first test, the energy was calculated as a function of volume for several bulk structures, using the parameters of Table I. The results are shown in Fig. 3. (Similar tests applied to several previous model potentials are described in Ref. 3; see also Ref. 17.) One dramatic shortcoming of the present potential arises with β -tin, which is experimentally the first new phase to appear with increasing pressure. This structure is shown as a dotted line in Fig. 3. The energy is somewhat too high, the equilibrium volume too large, and the bulk modulus too large. As a result, this structure would not be even a close competitor for the high pressure phase, according to the model.

Some tests revealed that the problem arises from interactions with the second neighbors in β -tin, which has six atoms in the first-neighbor shell. A similar problem arises for bcc, although that structure is of less interest here. Reducing the cutoff parameters to $R=2.75 \text{ \AA}$ and $D=0.1 \text{ \AA}$ results in the solid curve in Fig. 3, which is in much better agreement with the LDA calculations.⁸ (Other structures shown in Fig. 3 are unaffected by this change, except bcc, which is somewhat improved.) A similar improvement can be obtained by choosing $\alpha=0.001$ and $\lambda_3=4 \text{ \AA}^{-1}$. Other effects of these alternative parameter choices are discussed briefly in the following.

Since a plot such as Fig. 3 is not appropriate for sys-

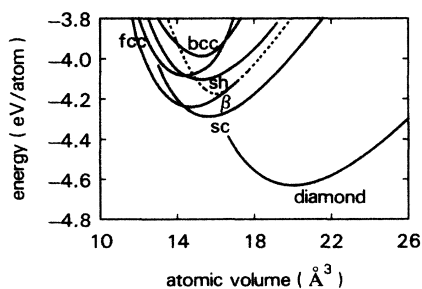


FIG. 3. Calculated cohesive energy vs volume per atom of silicon in the diamond, simple cubic (sc), β -tin (β), simple hexagonal (sh), bcc, and fcc structures. For β -tin, the dotted curve shows the result of the potential as given in Table I, while the solid curve results from taking $R=2.75 \text{ \AA}$ and $D=0.1 \text{ \AA}$, as discussed in text.

tems with very low coordination number, Fig. 4 gives the energy versus coordination number for the present model, just as in Fig. 2. From a chemical viewpoint, the bond length is a particularly crucial property, which is intimately related to the bond order. Figure 5 shows bond length versus coordination number for the same high-symmetry structures as in Fig. 4.

The model here is seen in Figs. 4 and 5 to describe rather well the variation of bonding and bond length with coordination. Even the dissociation energy and vibrational frequency of the Si_2 molecule are in reasonable agreement with experiment. Thus, in contrast to other^{1,3} empirical three-body potentials, the two-body part of the present potential gives a good description of the real two-body system. The hypothetical graphitic structure is also described rather well except for the complete absence of long-ranged interlayer forces in this model. For both graphitic and molecular silicon, the bond contraction relative to the bulk is qualitatively correct, though somewhat underestimated.

Another natural test is the calculation of elastic constants and phonon energies in the diamond structure. Such calculations have been performed by Heggie,²⁰ and his results are simply quoted here. The elastic constants are $c_{11}=121 \text{ GPa}$, $c_{12}=86 \text{ GPa}$, $c_{44}=10 \text{ GPa}$, and $\zeta=0.83$ which should be compared with experimental values of 166, 64, 80, and 0.54, respectively. The only indication of a significant problem is the exceedingly small value of c_{44} , which reflects the very weak bond-angle forces in this potential.

The calculated²⁰ phonon dispersion curve is shown in Fig. 6, along with experimental data. The overall agreement is rather good, considering that no phonon data were included in the fitting procedure. Again, the weak bond-angle forces are reflected in the low energies of the zone-edge transverse acoustic phonons. While these soft bond-angle forces are no doubt acceptable in many applications, anyone using this potential should certainly consider whether an accurate description of shear displacements or other strictly angular distortions is essential to their problem.

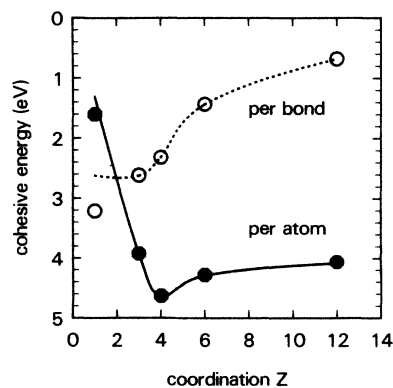


FIG. 4. Cohesive energy vs coordination number for potential (2)–(5). Solid line, energy per atom; dotted line, energy per bond. Lines are spline fits to results for high-symmetry structures as in Fig. 1. Circles represent *ab initio* results (Ref. 8).

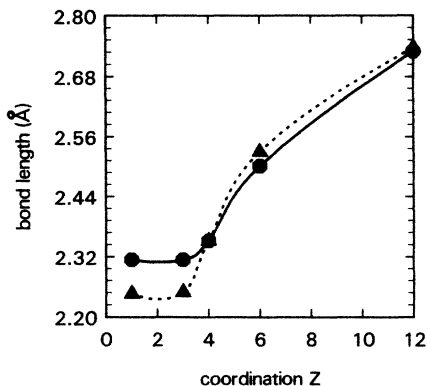


FIG. 5. Bond length vs coordination number for potential (2)–(5) (circles) compared with *ab initio* results (Ref. 8) (triangles) for high-symmetry structures as in Fig. 1. Lines are spline fits to guide the eye.

A particularly stringent test is the calculation of energies of point defects. Reliable experimental data is not available in this case, so one must rely on calculated formation energies. Several groups have reported LDA calculations of defect-formation energies,¹² with an accuracy of around ± 1 eV. In obtaining results of the present model for comparison, the atomic relaxations were calculated with a relatively crude scheme, so the formation energies reported here represent an upper bound, with a numerical accuracy of typically 0.1 or 0.2 eV in highly distorted cases.

The calculated vacancy-formation energy here is 2.8 eV, which compares reasonably well with the value of 3.6–3.8 eV in Ref. 12. For the interstitial geometries denoted¹² *T*, *H*, and *B*, the respective energies calculated here are 5.8, 4.5, and 4.5 eV, which should be compared with LDA values¹² of around 5–6, 4–5, and 4–5 eV. Note that the trends are described exceptionally well, except for the vacancy. On the whole, these tests are very encouraging.

However, the simple vacancy was found not to be the vacancy configuration of lowest energy in this model. A “split” vacancy had an energy 0.6 eV lower than the simple vacancy for a 54-atom cell with periodic boundary

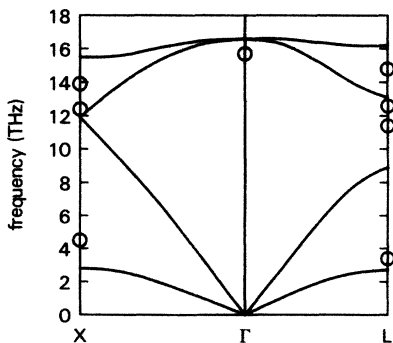


FIG. 6. Phonon dispersion curves calculated by Heggie (Ref. 20) with the present potential. Circles are experimental phonon energies.

conditions. Because of the large strain field of the split vacancy, the energy might be even lower for a truly isolated defect.

While such a split geometry has in fact been proposed²¹ as the ground state of the vacancy, experimental evidence²² suggests that the actual ground state is the simple vacancy. Since the split geometry avoids dangling bonds at a high cost in strain energy, the underestimation of bond-bending forces in the present parametrization could easily cause an underestimation of the formation energy of the split vacancy.

While many calculations of defect energies have been motivated by the problem of self-diffusion in silicon, Pandey²³ recently proposed a “concerted exchange” mechanism for self-diffusion which does not require the presence of defects. The energy of the saddle-point configuration in that process, i.e., the barrier for self-diffusion, is calculated here (for a 24-atom cell) to be 4.5 eV, in fortuitously good agreement with Pandey’s *ab initio* result of 4.3 eV. When a shorter cutoff is used, as suggested above for β -tin, the barrier here is reduced to 3.7 eV. This is still a very satisfactory agreement. On the other hand, for either cutoff the energies along the proposed diffusion path are substantially distorted, leading to a grossly inaccurate entropy for diffusion.²⁰

In a very different test, Metzler and Sabochick²⁴ performed zero-pressure molecular-dynamics simulations with this potential up to a temperature of 1200 K. They found that the system has a negative coefficient of thermal expansion. Relative to $T=0$ K, the linear contraction was roughly 0.03% at 300 K, and 0.5% at 1000 K. However, the contraction disappeared upon steepest-descent quenching, and so it did not represent any change in bonding topology. Moreover, the bond lengths increased upon heating, as expected, and fourfold coordination was maintained, even while the volume per atom decreased.

Silicon does in fact exhibit thermal contraction over a substantial temperature range, roughly from 20 K to 120 K. This contraction is associated with excitation of transverse acoustic modes.²⁵ Since the energy of these modes is underestimated in the present model, due to the soft bond-angle forces, it is perhaps not surprising that they should dominate the thermal expansion over a wider range of temperature than in the real material. It appears that this thermal contraction will not represent an important shortcoming in most applications. The correct description of bond topology (energy for under- and over-coordinated atoms, etc.) is more important than an accurate description of bond-angle forces. Nevertheless, it is important to be aware of the implications of the overly soft bond-angle forces in the present parametrization.

In a final set of static tests, the potential was applied to calculate the energies of several surface reconstructions. For both (111) and (100) surfaces, the energy gained by surface relaxation was negligible, while the first interlayer spacing decreased by approximately 0.1 Å. The 2×1 dimer reconstruction of Si(100) gave a gain of 2.4 eV per dimer, with a dimer bond length of 2.31 Å, i.e., shorter than the bulk bond length. Both the bond length and en-

ergy are in rather good agreement with LDA calculations.⁹ However, for the 2×1 reconstruction of Si(111) proposed by Pandey,¹⁰ the model gave an energy 0.15 eV per atom higher than the relaxed 1×1 surface, in contrast to an energy 0.2 eV lower found by LDA calculations.

For the hypothetical $\sqrt{3} \times \sqrt{3}$ Si adatom geometry¹¹ on Si(111), the top and hollow threefold sites were both about 0.1 eV per adatom more favorable than the 1×1 surface. The 0.6 eV difference between the two sites found by Northrup¹¹ is not well described by this potential. However, the geometries, which involve substantial distortions, are described quite well.

In general, the present potential did not perform as well in describing surfaces as the earlier potential (6). Results for that potential were described in Ref. 4. Some rough tests (not described here) indicate that the results for surfaces here could be improved somewhat by taking $\lambda_3 = \lambda_1$ instead of $\lambda_3 = \lambda_2$. That change is not recommended for general simulations, since it is *ad hoc* and not well tested, and leads to a less accurate description of point defects.

As previously mentioned, the potential was also tested with alternative values for the cutoff parameters. With $R = 2.75 \text{ \AA}$ and $D = 0.1 \text{ \AA}$, the β -tin properties were dramatically improved, as shown in Fig. 3. Properties for the bcc structure were also somewhat improved. Other polytypes were little affected. Properties for point defects and surfaces tested here were slightly worse, but not enough to be very significant in the context of the overall accuracy.

Using the values of R and D in Table I, but with $\alpha = 0.001$ and $\lambda_3 = 4 \text{ \AA}^{-1}$, led to similar improvements in polytypes, but to slightly more severe worsening of point defects, than with the reduced cutoff distance. For example, the formation energy of the tetrahedral-site interstitial fell to 3.3 eV.

Finally, preliminary dynamical simulations of molten Si have been carried out by several workers.²⁶ The liquid state is not very well described by the present potential, which appears to impose too strong a tendency to fourfold coordination. It is not yet clear whether this behavior can be improved by a different treatment of the cutoff. It is worth remarking that others^{27,28} have found it convenient to intentionally alter earlier potentials so as to impose fourfold coordination in the melt, in order to achieve a better description of the amorphous state obtained upon subsequent quenching.

To summarize, the potential performed quite well in describing many properties of silicon, and the main shortcomings found during testing could be attributed to

two problems with the potential.

The first problem involved the somewhat abrupt and arbitrary nature of the cutoff of the potential with distance. Besides leading to a poor description of the β -tin phase, tests which were not described here indicated that the energies of certain defects could vary by almost 1 eV with reasonable changes in the cutoff. Also, when the energy was studied as a function of some atomic position (e.g., in order to determine an energy barrier for diffusion), the cutoff could sometimes introduce spurious energy minima or maxima. Probably these problems could be solved by an improved treatment of the cutoff. However, this remains to be demonstrated.

The second problem involves the overly soft bond-bending forces in the present model. In many situations, including defects and surface reconstructions, the favorable geometry is determined by a trade-off between the number of dangling bonds and the strain energy. By underestimating the strain energy, the present potential can easily favor the wrong geometry, as appears to be the case for the split vacancy. Thus while the potential is certainly adequate for many purposes, an improved treatment of the bond-angle forces [which are included in a somewhat *ad hoc* way in (5a)] is highly desirable.

VI. CONCLUSIONS

There has already been considerable work on developing an empirical interatomic potential for silicon.¹⁻⁶ While the specific parametrization proposed here may be more accurate than previous potentials, this is by no means certain. The ultimate test is the usefulness of the potential in simulating properties of interest for silicon.

The central contribution here is, however, not the specific parametrization for silicon, but rather a general approach to constructing interatomic potentials, which goes beyond the usual three-body form. It is my hope that this approach may form the basis for developing interatomic potentials for a wide class of materials. In particular, the relatively good transferability of the present potential makes it appropriate for cases where the database of known properties is very limited.

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