Interatomic Potentials for Silicon Structural Energies

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We develop two- and three-body classical interatomic potentials that model structural energies for silicon. These potentials provide a global fit to a data base of first-principles calculations of the energy for bulk and surface silicon structures which spans a wide range of atomic coordinations and bonding geometries. This is accomplished by use of a new "separable" form for the three-body potential that reduces the three-body energy to a product of two-body sums and leads to computations of the energy and atomic forces in n^2 steps as opposed to n^3 for a general three-body potential.

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There is a great deal of current interest in the computer-based microscopic description of the structure and properties of materials. First-principles quantum-mechanical calculations, for example, have recently enjoyed great success in predicting the properties of simple structures.[1] There are many problems of great interest, however, for which molecular dynamics or simulated annealing studies are required, involving as many as 10^2–10^3 atoms moving through 10^4–10^6 configurations. These include melting, crystal growth and epitaxy, laser annealing, defect motion and materials strength, amorphous structures, and surface and interface reconstruction. The computational complexity of quantum-mechanical energies and forces precludes their use for such purposes for the foreseeable future. For simple systems such as rare-gas solids and liquids a sum of classical pair potentials yields acceptably accurate energies in acceptable computational times. Of necessity, two-body models have been extended to materials where their accuracy is highly questionable.

For covalent materials such as Si, pair potentials alone are inadequate, since the equilibrium diamond lattice is unstable relative to close-packed structures without three-body forces.[2] In fact, a three-body model fitted to small distortions of the diamond structure[3] has been used extensively to compute energies of complex Si structures, sometimes far beyond the range of its validity. Our goal here is to explore the extent to which a classical potential model for a covalent material *can* succeed in providing a global description of its structural energies. For this purpose, we exploit the huge computational effort that has produced accurate quantum-mechanical energies for simple Si structures spanning a wide range of atomic coordinations, bond lengths, and bond angles.[1,4] While only a few of these structures have low enough energies to be experimentally accessible in extended form, their features may occur as local distortions or dynamic intermediates associated with complex structures or processes. There are neither *a priori* arguments nor empirical tests to suggest that a classical model can accomplish such a global fit without arbitrarily many multiatom potentials. The computational complexity of such a model would render it impractical, and so we have confined our explorations to two- and three-body potentials. We find that it is possible to achieve excellent qualitative separation of structural groups, and quantitative accuracy for individual structures which should be acceptable for many purposes. This represents a significant step towards the performance of accurate simulations of technologically important semiconductor materials.

We have also achieved a major reduction in the computational complexity of the three-body model which is a considerable aid for simulation purposes. We introduce a new "separable" form for the potential which permits the energy to be calculated in n^2 computational steps instead of the n^3 steps generally required, where n is the number of interacting atoms.

Our two and three-body model is defined by the following expression for the structural energy:

$$E=\frac{1}{2}\sum_{1,2}{}^{\prime} V_2(1,2)+\sum_{1,2,3}{}^{\prime} V_3(1,2,3), \tag{1}$$

where primes indicate that all summation indices are distinct. Any three-body potential $V_3(1,2,3)$ may be expressed as a function of two lengths r_{12}, r_{13} and the included angle θ_1. This potential is symmetrized over the three particles in the sums in (1). We can expand the angular dependence of this potential in the complete set of Legendre polynomials without loss of generality. The coefficients in this expansion are functions F_l of bond lengths multiplied by linear coefficients C_l,

$$V_3(r_{12},r_{13},\theta_1)=\sum\nolimits_l C_l F_l(r_{12},r_{13})P_l(\cos\theta_1). \tag{2}$$

Our key simplification is to assume that the functions F_l are separable and symmetric products of functions ϕ_l of each bond length. This simplification can be motivated by the following physical picture of three-body interactions: Bonding interactions with atom 2 "tie up" some of the atomic orbitals of atom 1. The constrained atom 1 has modified bonding interactions with atom 3. The constraints must be cylindrically symmetric about the 1-2 axis, and have strengths which are functions of r_{12}. The constrained interactions are functions of r_{13}, and the simplest way of representing the symmetry of the system is to make the "constraining" and "interacting" functions equal for each l. This leads to the symmetric separable form

$$V_3(r_{12},r_{13},\theta_1) = \textstyle\sum_l C_l \phi_l(r_{12}) \phi_l(r_{13}) P_l(\cos\theta_1). \tag{3}$$

The addition theorem for spherical harmonics now reduces the three-body energy to the expectation value of a diagonal matrix between vectors Φ_{lm} that are simple two-body sums, i.e.,

$$\sum_{2,3} V_3(r_{12},r_{13},\theta_1) = \sum_l C_l \left[\frac{4\pi}{2l+1}\right] \sum_{m=-l}^{+l} \Phi^{*1}_{lm}\Phi^{1}_{lm}, \tag{4}$$

where

$$\Phi^j_{lm} = \textstyle\sum_2 \phi_l(r_{j2})\, Y_{lm}(\hat{\mathbf{r}}_{j2}). \tag{5}$$

The Φ^j_{lm} vectors represent the moments of the structure around atom j. Equation (4) is not the correct sum to substitute in (1) because we have ignored the "prime" condition on the summation indices, $2 \neq 3$. The correction introduces a modification of the two-body interaction,

$$\sum_{2,3}{}' V_3(r_{12},r_{13},\theta_1) = \sum_{2,3} V_3(r_{12},r_{13},\theta_1) - \sum_2 f_3(r_{12}), \tag{6}$$

where

$$f_3(r) = \textstyle\sum_l C_l \phi_l^2(r). \tag{7}$$

Previous work with classical models for Si beyond the restricted Keating model[3] includes that of Stillinger and Weber (SW),[5] and Pearson, Takai, Halicioglu, and Tiller (PTHT).[6] The three-body potentials used by SW are separable (although the separability was not utilized in their work), and have a Keating[3] angular form ($\frac{3}{2}C_0 = C_1 = C_2$; $C_3, C_4, \ldots = 0$). The potentials were confined within a very small cutoff radius of 3.78 Å. Their nine parameters were adjusted to fit the bond length, cohesive energy, and melting temperature of bulk diamond Si, and satisfy other qualitative criteria.[5] Alternatively, PTHT[6] used the nonseparable Axilrod-Teller three-body potential[7] which is based on the generalization of van der Waals fluctuating-dipole forces for three particles. These potentials were long ranged with algebraic decays [$V_3(r) \approx r^{-9}$]. The three-parameter PTHT potential was obtained through an average fit to the bond lengths and cohesive energies of bulk diamond Si and molecular Si_2.

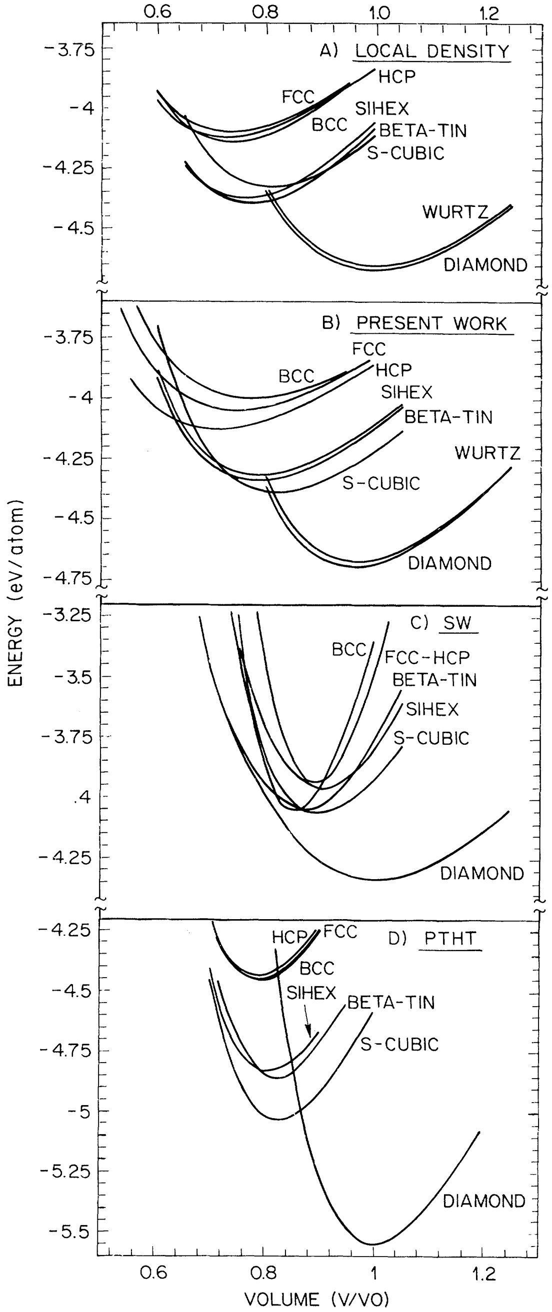

FIG. 1. Energies for simple silicon structures as a function of atomic volume. SW potentials are from Ref. 5, and PTHT from Ref. 6. Wurtzite could not be distinguished from diamond in (c) and (d).

The quantum-mechanical Si data base includes energies of diamond, wurtzite, the high-pressure β-tin and simple hexagonal structures, and simple hypothetical Si structures[1,4,8] as shown in Fig. 1(a). To account for bond breaking energies, we have added to the data base our own linear augmented-plane-wave calculations for the energy of a four-layer Si(111) slab as a function of the positions of the outermost atomic layers (Fig. 2). Because of symmetry, only moments Φ_{lm} with certain values of the angular momentum l are allowed for each structure, e.g., the $l=0,3,4,6,\ldots$ moments are allowed in diamond. The (111) slab is the only structure in the above data base that permits an $l=1$ moment and is therefore essential to the fit.

We have examined a few short-range, monotonic functional forms for the three-body functions ϕ along with similar functions for the two-body potential. We were unable to find satisfactory fits with very short-range functions of the type used by SW.[5] Very general functional forms for ϕ_l often led to unphysical solutions that provided good fits but performed poorly on test structures. Overall, our best results were obtained with the family of simple exponentials, $\phi_l = e^{-\alpha_l r}$. In conjunction, we used generalized Morse two-body potentials,

$$V_2(r) = A_1 e^{-\lambda_1 r} + A_2 e^{-\lambda_2 r}. \qquad (8)$$

For our potential, the decays α_l, λ_1, and λ_2 of the radial functions are nonlinear parameters, whereas the coefficients C_l, A_1, and A_2 are linear variables. The parameters in the potential were least-squares fitted to the data base energies over the entire range of atomic volume spanned by each curve in Fig. 1. For the fit we selected a subset of structures from Fig. 1 that contained all of the angular momentum components up to $l=6$. We typically constrained the higher l's to a single decay rate.

The results of our fit compare very well with the quantum-mechanical energies for the Si(111) slab, as shown in Fig. 2. Our global fit to the crystal structures shown in Fig. 1(b), agrees with the quantum-mechanical results of Fig. 1(a), to within an rms error of 0.05 eV and displays the correct structural trends over a large range of atomic volumes. The absolute energies are plotted in Figs. 1 and 2. In Fig. 1(b), the bcc and hexagonal-Si phases were test structures that were not fitted. Hexagonal-phase Si is very close to β-tin, as it should be.[4] Wurtzite is higher in energy than diamond-phase Si. The hcp phase is not as well fitted as other phases and the simple cubic phase is somewhat lower in energy than the quantum-mechanical result. The first high-pressure phase is correctly predicted to be β-tin. Our diamond-phase Si has an equilibrium bond length of 2.32 Å (experimentally 2.351 Å), but the nonlinear decay parameters could be uniformly scaled to produce the experimental bulk bond length if desired.

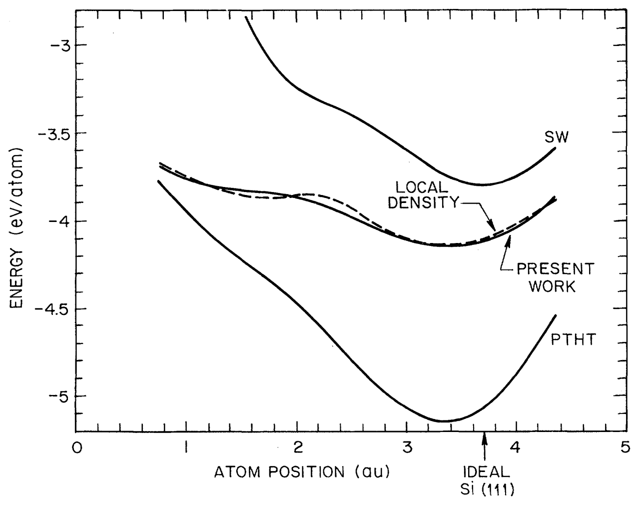

FIG. 2. Energy of a four-layer Si(111) slab. Starting from the ideal (111) geometry the two outermost layers are symmetrically displaced in the normal direction. The distance of either layer from the slab center is plotted. At 2.22 a.u., the slab reduces to two graphitic atomic planes.

The parameters for our fitted potential are listed in Table I. The solution is stable, remaining within the same range of parameters when the weights or structures in the fitting data base are altered, or when the number of three-body nonlinear parameters is altered by 1. The coefficients in the angular expansion (C_l) decay uniformly, indicating the convergence of the solution and a well-defined angular decomposition. Further, the range of the potentials is comparable to that of the atomic valence wave-function overlaps, indicating a physical reasonableness in the overall fit. Cutting off all **r** sums at 10 Å only causes an error of order 0.01 eV in the total energies.

The structural energies, from the previously obtained two- and three-body Si potentials of SW[5] are plotted in Fig. 1(c) and in Fig. 2, whereas those from the potentials of PTHT[6] are shown in Fig. 1(d) and in Fig. 2.[9] Clearly from Figs. 1 and 2, the present potentials compare with the quantum-mechanical results

TABLE I. The values of the parameters for the present two- and three-body potentials. λ_l and α_1, α_2 are nonlinear decay parameters; C_l and A_1, A_2 are the linear coefficients.

	l,i	α_i, λ_l (Å^{-1})	A_i, C_l (eV)
Two-body	1	3.946 668	$0.268\,2936 \times 10^5$
	2	1.191 187	$-0.425\,9863 \times 10^2$
Three-body	0	1.246 156	$0.913\,9775 \times 10^2$
	1	1.901 049	$0.164\,4013 \times 10^5$
	2	1.786 959	$0.958\,0299 \times 10^4$
	3	1.786 959	$0.666\,3147 \times 10^4$
	4	1.786 959	$0.398\,7710 \times 10^4$
	5	1.786 959	$0.204\,6722 \times 10^4$
	6	1.786 959	$0.701\,8867 \times 10^3$

much better than previous work. The grouping of structures into three energy classes and the values of their equilibrium volumes are improved compared to SW, and the compressibilities and energy differences between the classes are improved compared to PTHT.

The three-body potential emerging from the fits has (for $r_{12}=r_{13}=2.35$ Å) a very weak dependence on the angle for $90° \lesssim \theta \leq 180°$, with a very shallow minimum at $\theta \cong 110°$–$115°$. There is a very strong repulsion between bonds for $\theta \leq 70°$. The two-body potential has a minimum at $R \simeq 2.77$ Å, with a depth of $E = -1.09$ eV at the minimum. Clearly this pair potential is inappropriate for the multiply bonded Si_2 dimer. These properties of our two-body potential are consistent with the work of Carlsson, Gelatt, and Ehrenreich,[10] who quite generally showed that pair potentials in simple metals are significantly weaker than the cohesive energy, and have a minimum at separations larger than the equilibrium bond length. Our attempts to constrain our two-body potential to fit Si_2 did not yield satisfactory fits to the structural energies. We believe that a model which simultaneously fits small clusters and extended systems must include N-body potentials beyond $N=3$.

Further tests with the present potentials yield a vacancy formation energy of 4.82 eV in comparison with the quantum-mechanical result of ≈ 4.5 eV.[11] Symmetric dimers are found for a relaxed Si(100) surface, with bond length $\cong 2.50$ Å, and an energy gain of 1.22 eV/dimer relative to the ideal surface. The model is too stiff relative to small distortions around the diamond structure, with some photon frequencies 25% to 50% too high.

Atomic forces, necessary for many purposes, can also be obtained in n^2 calculational steps. By differentiation of (4) and use of suitable identities, the force on atom k due to the three-body potential is

$$\mathbf{F}_k^{(3)} = -\sum_l C_l \left(\frac{4\pi}{2l+1}\right) \sum_{m=-l}^{+l} \sum_j \mathbf{f}_{lm}(\mathbf{r}_{kj}) [\Phi_{lm}^{*k} + (-1)^l \Phi_{lm}^{*j}] + \mathrm{c.c.} - 4 \sum_l C_l \sum_j \phi_l(r_{kj}) \frac{\partial \phi_l(r_{kj})}{\partial r_{kj}} \frac{\mathbf{r}_{kj}}{r_{kj}}. \tag{9}$$

In the above,

$$\begin{aligned} \mathbf{f}_{lm}(\mathbf{r}) = \frac{\partial \phi_l(r)}{\partial r} Y_{lm} \hat{\mathbf{e}}_r + \frac{\phi_l(r)}{2r} \{ & [(l+m+1)^{1/2}(l-m)^{1/2} Y_{l,m+1} e^{-i\phi} - (l-m+1)^{1/2}(l+m)^{1/2} Y_{l,m-1} e^{i\phi}] \hat{\mathbf{e}}_\theta \\ & + 2i(m \sin\theta) Y_{lm} \hat{\mathbf{e}}_\phi - \cos\theta [(l+m+1)^{1/2}(l-m)^{1/2} Y_{l,m+1} e^{-i\phi} \\ & + (l-m+1)^{1/2}(l+m)^{1/2} Y_{l,m-1} e^{i\phi}] \hat{\mathbf{e}}_\phi \}, \end{aligned} \tag{10}$$

where (r, θ, ϕ) are the $\mathbf{r}$ spherical coordinates, $(\hat{\mathbf{e}}_r, \hat{\mathbf{e}}_\theta, \hat{\mathbf{e}}_\phi)$ are spherical unit vectors, and Y_{lm} have arguments θ, ϕ. The force calculation requires a prior computation of the Φ_{lm} vectors.

In conclusion, we have described a new "separable" form for the three-body potential that leads to efficient energy and force calculations. We have developed two-body and separable three-body interatomic potentials for Si which can interpolate among first-principles energy calculations for both semiconducting and metallic structures, and improve upon previous classical Si models. Classical potentials such as the present one may be extended to compound semiconductors, and have a potentially wide range of applications in simulations of materials properties.

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