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Pair potentials for C–C, Si–Si and Si–C from inversion of the cohesive energy

Wang Jian, Zhang Kaiming and Xie Xide

China Centre of Advanced Science and Technology (World Laboratory), PO Box 8730, Beijing, and Department of Physics, Fudan University, Shanghai 200433, People's Republic of China

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Abstract. The Carlsson–Gelatt–Ehrenreich inversion technique is applied to the derivation of pair potentials for the elemental bonds C–C and Si–Si, and the compound bond Si–C. Chen's Möbius function method is used to speed up the convergency. The cohesive energies are obtained from the *ab initio* pseudopotential total energy calculation of Chang and Cohen within the framework of the local-density approximation and fitted to the universal binding energy function of Rose *et al.* The pair potentials thus obtained reproduce exactly the full cohesive energy curves, lattice constants and bulk moduli.

1. Introduction

It is most helpful to atomic simulation if the interatomic potential can be expressed pairwise, in the same way as the Lennard-Jones potential used in van der Waals solids, and the Morse potential used in metals. Nowadays, an efficient method has been developed to derive exactly pair potentials from experiments or accurate cohesive energies [1]. The method was originally developed by Carlsson, Gelatt and Ehrenreich (CGE) [2] and improved by Chen and Ren [1] using the Möbius inversion procedure. The method has been used to derive pair potentials for copper by Mookerjee *et al.* [3]. In general, there are additional terms which cannot be expressed pairwise in the cohesive energy [4, 5], such as the bond energy in the tight-binding bond model [5]. However, as long as one can calculate these terms independently and leave the pair terms on one side of equation, the method to derive the pair terms is the same. The merits of the method are that no fitting parameter is needed and the full cohesive energy function is reproduced, instead of only the equilibrium points as in the case of the empirical methods. In this paper, we apply the method to the Si–C system. The system is interesting because using this method for the diamond-like structure and for a compound system has not been tackled before. However, as previously [1, 2], no effort is made to evaluate the non-pairwise terms in the cohesive energy, which is still an active field. The effects of neglecting these terms have been discussed together with the limitation of pair potentials [6, 7].

2. Method

Our starting point is that the cohesive energy is expressed as a sum of radial pair potentials as follows:

$$E_{\text{coh}}(r_1) = \frac{1}{2} \sum_{p=1}^{\infty} n_p \phi(S_p r_1) \quad (1)$$

where n_p is the number of p th-neighbour atoms at the distance $S_p r_1$ from the atom at origin and r_1 is the nearest-neighbour distance. For a given lattice, n_p and S_p can be easily determined. For example, for the diamond structure, one obtains

$$\begin{aligned}
 E_{\text{coh}}(r_1) = & \sum_{s=1}^{\infty} 3\phi(sr) + \sum_{s=1}^{\infty} \sum_{t=1}^{\infty} 6 \left\{ \phi \left[\sqrt{s^2 + t^2} r \right] + \phi \left[\sqrt{\left(s - \frac{1}{2}\right)^2 + \left(t - \frac{1}{2}\right)^2} r \right] \right\} \\
 & + \sum_{s=1}^{\infty} \sum_{t=1}^{\infty} \sum_{u=1}^{\infty} 4\phi \left(\sqrt{s^2 + t^2 + u^2} r \right) + 2\phi \left[\sqrt{\left(s - \frac{1}{4}\right)^2 + \left(t - \frac{1}{4}\right)^2 + \left(u - \frac{1}{4}\right)^2} r \right] \\
 & + 2\phi \left[\sqrt{\left(s - \frac{3}{4}\right)^2 + \left(t - \frac{3}{4}\right)^2 + \left(u - \frac{3}{4}\right)^2} r \right] \\
 & + 12\phi \left[\sqrt{\left(s - \frac{1}{2}\right)^2 + \left(t - \frac{1}{2}\right)^2 + u^2} r \right] \\
 & + 6\phi \left[\sqrt{\left(s - \frac{1}{4}\right)^2 + \left(t - \frac{3}{4}\right)^2 + \left(u - \frac{3}{4}\right)^2} r \right] \\
 & + 6\phi \left[\sqrt{\left(s - \frac{3}{4}\right)^2 + \left(t - \frac{1}{4}\right)^2 + \left(u - \frac{1}{4}\right)^2} r \right] \quad (2)
 \end{aligned}$$

where $r = 4r_1/\sqrt{3}$. Thus $S_1 = 1$, $n_1 = 4$, $S_2 = 2\sqrt{2}/\sqrt{3}$, $n_2 = 12$, etc.

The method is formally as follows. Expressing equation (1) as the operation of two operators T and U , gives

$$E_{\text{coh}}(r_1) = (T + U)\phi(r_1). \quad (3)$$

Then, if the inverse of T is obtainable, one finds that

$$\begin{aligned}
 \phi(r_1) = & (T + U)^{-1} E_{\text{coh}}(r_1) = (1 + T^{-1}U)^{-1} T^{-1} E_{\text{coh}}(r_1) \\
 = & (1 - T^{-1}U + T^{-1}UT^{-1}U - \dots) T^{-1} E_{\text{coh}}(r_1). \quad (4)
 \end{aligned}$$

In the original CGE paper, T was chosen as the operation to produce the first term of equation (1), i.e.

$$T\psi(r_1) = 1/2n_1\psi(S_1r_1) \quad (5)$$

and the inverse of T is

$$T^{-1}\psi(r_1) = 2/n_1\psi(r_1/S_1) \quad (6)$$

since

$$TT^{-1}\psi(r_1) = \psi(r_1). \quad (7)$$

The operation on U produces the sum of all the terms except $p = 1$ in equation (1).

Once the function $E_{\text{coh}}(r_1)$ is given, a pair potential can then be derived. In practice, the convergence of the series in equation (4) may be very slow. On the basis of the Möbius inversion formula, Chen and Ren [1] have demonstrated that a faster convergent series can be constructed by properly renormalizing the inverse operator T^{-1} . In the following, we

derive such an operator for the diamond structure. We decompose the contribution of atoms on the diagonal and define an operator T by

$$T\psi(r_1) = 2 \sum_{s=1}^{\infty} [\psi(sr_1) + \psi(4sr_1)] \tag{8}$$

and the operator U for the rest of equation (2) is

$$\begin{aligned} U\psi(r_1) = & \sum_{s=1}^{\infty} 3\psi(sr) - \psi((4s-2)r) \\ & + \sum_{s=1}^{\infty} \sum_{t=1}^{\infty} 6 \left\{ \psi\left(\sqrt{s^2+t^2}r\right) + \psi\left[\sqrt{\left(s-\frac{1}{2}\right)^2 + \left(t-\frac{1}{2}\right)^2}r\right] \right\} \\ & + \sum_{s=1}^{\infty} \sum_{t=1}^{\infty} \sum_{u=1}^{\infty} 12\psi\left[\sqrt{\left(s-\frac{1}{2}\right)^2 + \left(t-\frac{1}{2}\right)^2 + u^2}r\right] \\ & + 6\psi\left[\sqrt{\left(s-\frac{1}{4}\right)^2 + \left(t-\frac{3}{4}\right)^2 + \left(u-\frac{3}{4}\right)^2}r\right] \\ & + 6\psi\left[\sqrt{\left(s-\frac{3}{4}\right)^2 + \left(t-\frac{1}{4}\right)^2 + \left(u-\frac{1}{4}\right)^2}r\right] \\ & + \sum_{\text{excl.}} \sum_{s=t=u}^{\infty} 4\psi\left(\sqrt{s^2+t^2+u^2}r\right) \\ & + 2\psi\left[\sqrt{\left(s-\frac{1}{4}\right)^2 + \left(t-\frac{1}{4}\right)^2 + \left(u-\frac{1}{4}\right)^2}r\right] \\ & + 2\psi\left[\sqrt{\left(s-\frac{3}{4}\right)^2 + \left(t-\frac{3}{4}\right)^2 + \left(u-\frac{3}{4}\right)^2}r\right] \end{aligned} \tag{9}$$

where $r = 4r_1/\sqrt{3}$. To find T^{-1} , we define an operator N by

$$N\psi(r) = \frac{1}{2} \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} (-1)^{m-1} \mu(n) \psi(4^{m-1}nr) \tag{10}$$

where $\mu(n)$ is the Möbius function [8] defined by

$$\mu(n) = \begin{cases} 1 & \text{if } n = 1 \\ 0 & \text{if } n \text{ is divisible by a square} \\ (-1)^q & \text{if } n \text{ is the product of } q \text{ distinct primes.} \end{cases} \tag{11}$$

For example, $\mu(2) = -1$, $\mu(3) = -1$, $\mu(4) = 0$, $\mu(5) = -1$, $\mu(6) = 1$, etc. Then

$$\begin{aligned} NT\psi(r) &= \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \sum_{s=1}^{\infty} (-1)^{m-1} \mu(n) [\psi(4^{m-1}nsr) + \psi(4^mnsr)] \\ &= \sum_{n=1}^{\infty} \sum_{s=1}^{\infty} \mu(n) \psi(ns r) + \sum_{n=1}^{\infty} \sum_{s=1}^{\infty} \mu(n) \\ &\quad \times \left(\sum_{m=2}^{\infty} (-1)^{m-1} \psi(4^{m-1}nsr) + \sum_{m=1}^{\infty} (-1)^{m-1} \psi(4^mnsr) \right) \\ &= \sum_{n=1}^{\infty} \sum_{s=1}^{\infty} \mu(n) \psi(ns r). \end{aligned} \tag{12}$$

The Möbius inversion theorem states that if

$$F(r) = \sum_{n=1}^{\infty} f(nr) \quad (13)$$

then

$$f(r) = \sum_{n=1}^{\infty} \mu(n)F(nr) \quad (14)$$

and vice versa. This gives, from equation (12),

$$NT\psi(r) = \psi(r) \quad (15)$$

from which we obtain $T^{-1} = N$.

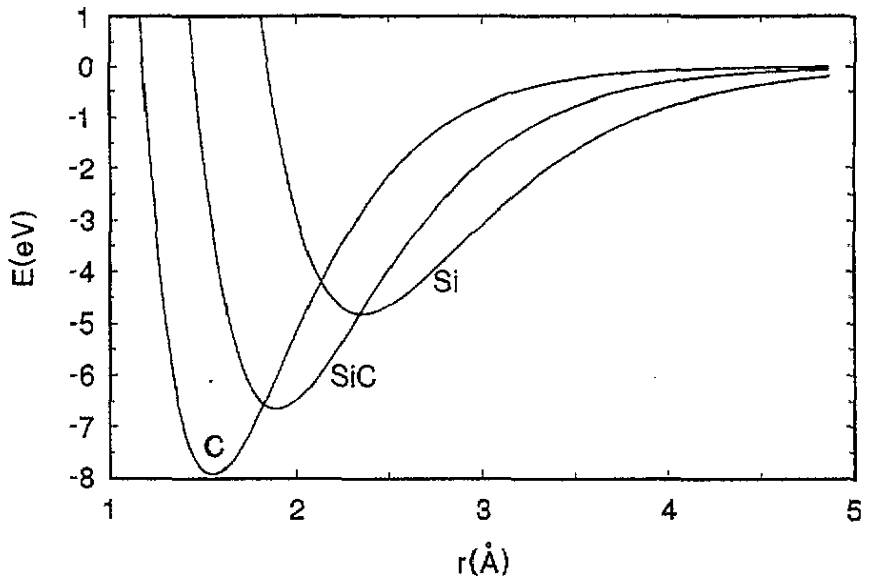


Figure 1. The cohesive energy curves of diamond C and Si, and also zincblende SiC fitted to the universal binding energy function of Rose *et al*.

Since now the operator T^{-1} contains far more information than the original form of equation (6), the convergence of equation (4) can be significantly faster. In the present calculation, the cohesive energy data are from the state-of-the-art *ab initio* pseudopotential total energy calculations within the framework of the local density approximation by Chang and Cohen [9]. They used Murnaghan's equation of state to display the energy curves. Since only points around the equilibrium minimum of the energy curve are faithfully given by Murnaghan's equation, we use instead the empirical universal binding energy function of Rose *et al* [10] to reduce the cohesive energy at large lattice constants. The form of the function used by Rose *et al* is

$$E_{\text{coh}}(r) = -E_c[1 + (r - r_e)/1] \exp[(r - r_e)/1] \quad (16)$$

where E_e is the binding energy at equilibrium nearest-neighbour distance r_e and l is a length scale related to the bulk modulus B by

$$l = \sqrt{\sqrt{3}E_e/24Br_e}. \tag{17}$$

The parameters E_e , r_e and B have been given by Chang and Cohen [9] and the parameters used in equation (16) are listed in table 1. The curves for cohesive energy are displayed in figure 1.

Table 1. Parameters used for the cohesive energy E_{coh} and pair potential ϕ curves fitted to the universal binding energy function of Rose *et al.*

	E_{coh}			ϕ		
	C	Si	SiC	C-C	Si-Si	Si-C
E_e (eV/atom)	7.94	4.84	6.66	1.766	1.245	1.318
r_e (Å)	1.544	2.352	1.888	1.920	2.789	2.320
B (Mbar)	4.38	0.92	2.12			
l (Å)	0.3686	0.5084	0.4385	0.358	0.495	0.432

The pair potential for the Si-C bond is derived from the zincblende-structured silicon carbide. In this structure, the cohesive energy per SiC pair may be written as

$$\begin{aligned}
 E_{\text{coh}}(r_l) = & \sum_{s=1}^{\infty} 3[\phi_{\text{CC}}(sr) + \phi_{\text{SiSi}}(sr)] \\
 & + \sum_{s=1}^{\infty} \sum_{t=1}^{\infty} 6 \left\{ \phi_{\text{CC}}(\sqrt{s^2 + t^2}r) + \phi_{\text{SiSi}}(\sqrt{s^2 + t^2}r) \right. \\
 & + \left. \phi_{\text{CC}} \left[\sqrt{(s - \frac{1}{2})^2 + (t - \frac{1}{2})^2}r \right] + \phi_{\text{SiSi}} \left[\sqrt{(s - \frac{1}{2})^2 + (t - \frac{1}{2})^2}r \right] \right\} \\
 & + \sum_{s=1}^{\infty} \sum_{t=1}^{\infty} \sum_{u=1}^{\infty} 4 \left[\phi_{\text{CC}}(\sqrt{s^2 + t^2 + u^2}r) + \phi_{\text{SiSi}}(\sqrt{s^2 + t^2 + u^2}r) \right] \\
 & + 12 \left\{ \phi_{\text{CC}} \left[\sqrt{(s - \frac{1}{2})^2 + (t - \frac{1}{2})^2 + u^2}r \right] \right. \\
 & + \left. \phi_{\text{SiSi}} \left[\sqrt{(s - \frac{1}{2})^2 + (t - \frac{1}{2})^2 + u^2}r \right] \right\} \\
 & + 4 \left\{ \phi_{\text{CSi}} \left[\sqrt{(s - \frac{1}{4})^2 + (t - \frac{1}{4})^2 + (u - \frac{1}{4})^2}r \right] \right. \\
 & + \left. \phi_{\text{CSi}} \left[\sqrt{(s - \frac{3}{4})^2 + (t - \frac{3}{4})^2 + (u - \frac{3}{4})^2}r \right] \right\} \\
 & + 12 \left\{ \phi_{\text{CSi}} \left[\sqrt{(s - \frac{1}{4})^2 + (t - \frac{3}{4})^2 + (u - \frac{3}{4})^2}r \right] \right. \\
 & + \left. \phi_{\text{CSi}} \left[\sqrt{(s - \frac{3}{4})^2 + (t - \frac{1}{4})^2 + (u - \frac{1}{4})^2}r \right] \right\}
 \end{aligned} \tag{18}$$

where $r = 4r_1/\sqrt{3}$. We use above-derived pair potential for C-C and Si-Si to calculate the terms ϕ_{CC} and ϕ_{SiSi} . If we move the terms ϕ_{CC} and ϕ_{SiSi} to the left-hand side of the equation, the derivation of ϕ_{CSi} is straightforward, as above. To use the Möbius inversion theorem, the operator T may be defined as

$$T\psi(r_1) = 4 \sum_{s=1}^{\infty} [\psi(sr_1) - \psi(2sr_1)]. \quad (19)$$

The operator U is then

$$\begin{aligned} U\psi(r_1) = & \sum_{\text{excl.}}^{\infty} \sum_{s=t=u}^{\infty} 4 \left\{ \psi \left[\sqrt{(s - \frac{1}{4})^2 + (t - \frac{1}{4})^2 + (u - \frac{1}{4})^2} r \right] \right. \\ & \left. + \psi \left[\sqrt{(s - \frac{3}{4})^2 + (t - \frac{3}{4})^2 + (u - \frac{3}{4})^2} r \right] \right\} \\ & + \sum_{s=1}^{\infty} \sum_{t=1}^{\infty} \sum_{u=1}^{\infty} 12 \left\{ \psi \left[\sqrt{(s - \frac{1}{4})^2 + (t - \frac{3}{4})^2 + (u - \frac{3}{4})^2} r \right] \right. \\ & \left. + \psi \left[\sqrt{(s - \frac{3}{4})^2 + (t - \frac{1}{4})^2 + (u - \frac{1}{4})^2} r \right] \right\} \end{aligned} \quad (20)$$

where $r = 4r_1/\sqrt{3}$. The inverse of T is obtained as

$$T^{-1}\psi(r) = \frac{1}{4} \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \mu(n)\psi(2^{m-1}nr). \quad (21)$$

The remaining procedure is to use equation (4) as above for ϕ_{CC} and ϕ_{SiSi} .

3. Results and discussion

The results of the potentials are displayed in figure 2. One observes that the minimum of the pair potential lies at a longer distance than that of the cohesive energy curve, and the nearest neighbours are repulsive since $d\phi/dr < 0$. This was also observed by CGE for the elements of FCC Cu, and BCC K and W [2]. The shape of the potential curve is quite similar to the cohesive energy curve and it also fits equation (16) well; so we have also listed the fitting parameters in table 1. Since *ab initio* pseudopotential total energy calculations are not available for large distances and the cohesive energy used in inversion in this range depended on the universal binding energy function of Rose *et al*, this means that the present pair potentials are not sufficiently accurate. Depending on more *ab initio* data and including additional higher-order terms of $(r - r_e)/l$ in the function of Rose *et al* [10] in equation (16), the situation may be improved. Since the procedure is reversible, all the information in the full energy function, such as the binding energy E_e , the equilibrium nearest-neighbour distance r_e and the bulk modulus B in equation (16), is reproducible.

Some results can be inferred from the radial pairwise potentials. For example, since the nearest neighbours are repulsive ($d\phi/dr < 0$), relaxation in the first interlayer spacing at the surface will result in an expansion in the vacuum. However, this may not be true in the real case, such as for Si [11]. Carlsson and co-workers [2, 6, 7] have discussed other results of the pairwise potentials, such as the facts that pairwise potentials always produce

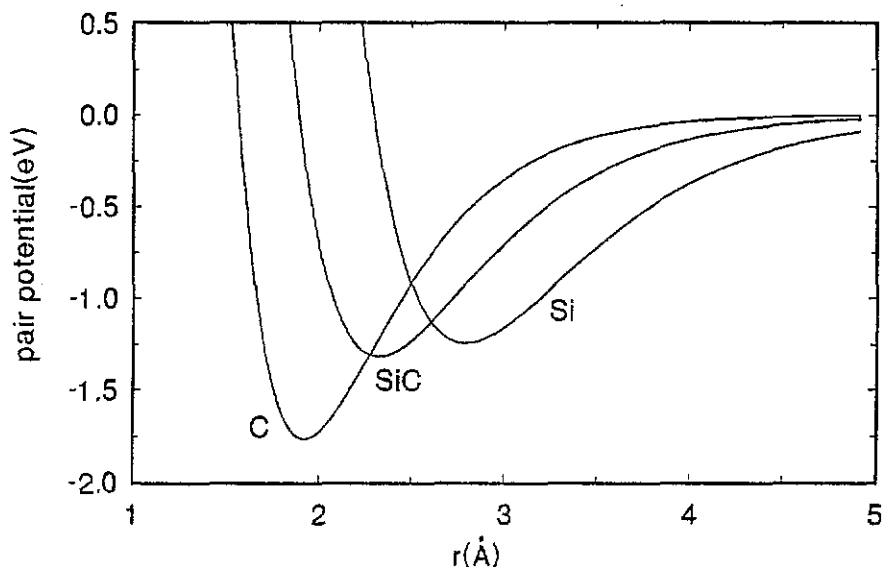


Figure 2. The pair potential curves for the C-C, Si-Si, and Si-C bonds.

a vanishing Cauchy pressure $C_{12}-C_{44}$ and are preferable to close-packed structures. For a more accurate description of interatomic potentials, the cohesive energy preferably should explicitly include volume-dependent terms and many-body-dependent terms [4, 5, 12]. It is preferable to calculate such terms *ab initio*. Then the way in which to use the present method to derive pair potentials is to merge these terms with the cohesive energy and to leave only the pairwise terms on one side of the equation. This procedure may be useful for part of the pair potentials in the tight-binding approximation of cohesive energy [5, 13].

In conclusion, the CGE inversion method for pair potentials improved by Chen's Möbius function system method has been applied to diamond-like structures and specifically to the compound system Si-C.

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