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LETTER TO THE EDITOR

On the transferable SETB method for Si

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Abstract. The two types of transferable semi-empirical tight-binding (SETB) method for Si recently proposed by Goodwin *et al* and by Sawada, which are intended to reproduce the binding energies and equilibrium volumes of variously coordinated structures of Si, have been examined and compared with each other. It has been found that there are some drawbacks in the method proposed by Goodwin *et al*, and that the method proposed by Sawada is much superior. The parameters in the Sawada method have been readjusted in order to apply this method to lattice defects or disordered systems of Si. The present results indicate the importance of incorporating the dependence on the local environment into the repulsive energy in the transferable SETB method. This can be explained by the origin of the repulsive energy.

Theoretical methods of investigation of atomic structures and total energies of complex systems of Si, such as dislocations, surfaces, grain boundaries, amorphous structure and clusters can be classified into the following three groups. The first group contains the *ab initio* methods based on the density-functional theory, which can give very reliable results. However, the drawbacks are the limited numbers of tractable atoms and the consumption of computing power even in the recent effective algorithm [1]. The second group contains the methods using inter-atomic potentials. Recently, various types of inter-atomic potentials beyond pair potentials have been proposed for Si, where the many-body terms or the dependence on the local environment are incorporated [2–5]. These potentials are constructed, in general, so as to reproduce the total energies and atomic structures of a wide range of phases of Si obtained by the methods of the first group [6]. However, it is not certain that potential forms and parameters are applicable to any local environment because this type of method does not deal directly with the change in electronic structure.

The third group of theoretical methods are those where total energies and atomic structures are given via semi-empirical calculations of electronic structures. This type of method intervenes between the former two groups. The semi-empirical tight-binding (SETB) method [7] is most widely used for Si in this group. This method can deal with a fairly large number of atoms by virtue of simple expressions of electronic structures and total energies and has been successfully used for various systems of Si. However, one of the most serious problems in this method is that the transferability for structures other than fourfold-coordinated ones is not necessarily guaranteed. For example, it is well known that the binding energies and equilibrium volumes of close packed structures of Si are poorly reproduced in the SETB method and in similar methods [8, 9]. If this problem

were overcome, the applicability of this type of theoretical method would be greatly extended.

Recently, for this purpose, two types of transferable SETB method have been proposed independently. One was proposed by Goodwin *et al* [10] and the other was proposed by Sawada [11]. Both methods are intended to reproduce the binding energy–volume curves of various structures of Si given by the density-functional theory [6]. In both methods, the behaviour of the two-centre hopping integrals and the inter-atomic repulsive potentials for large distances is modified and these are smoothly truncated by attenuation functions. In addition, in the method of Sawada, the dependence on the local environment is incorporated in the repulsive energy through the effective coordination numbers. In the present letter, these two types of transferable SETB method for Si are examined and are compared with each other in view of applying them to lattice defects or disordered systems of Si. As will be shown later, it has been found that the method of Sawada is much superior to the method of Goodwin *et al*, and this can be explained by the origin of the repulsive energy in the SETB method.

In the framework of the SETB method [7, 8, 12], the binding energy, which is the difference between the total energies of the system and the free atoms, is expressed as a sum of the band structure energy E_{bs} and the remaining repulsive energy E_{rep} . E_{bs} is a sum of occupied eigen energies calculated via the tight-binding approximation, and E_{rep} is usually expressed as a sum of short-range inter-atomic repulsive potentials. The two-centre hopping integrals $V_{ll'm}$ in the tight-binding Hamiltonian are usually expressed as $V_{ll'm}^0(r_0/r)^n$. r is the inter-atomic distance, r_0 is the equilibrium distance in diamond Si, and n is usually 2 [7, 12]. The pairwise repulsive potential is expressed, for example, as $\varphi(r_0)(r_0/r)^m$, where m is 4 or 5 [8, 13, 14].

Goodwin *et al* [10] have proposed that the representation of the equilibrium volumes of close packed structures of Si is improved by using the following functional forms for the two-centre hopping integrals and the repulsive potential:

$$V_{ll'm}(r) = V_{ll'm}^0 \left(\frac{r_0}{r}\right)^n \exp \left[n \left\{ -\left(\frac{r}{r_c}\right)^{n_c} + \left(\frac{r_0}{r_c}\right)^{n_c} \right\} \right] \quad (1)$$

and

$$\varphi(r) = \varphi(r_0) \left(\frac{r_0}{r}\right)^m \exp \left[m \left\{ -\left(\frac{r}{r_c}\right)^{n_c} + \left(\frac{r_0}{r_c}\right)^{n_c} \right\} \right]. \quad (2)$$

These functional forms are those constructed by multiplying the usual forms by smoothed step functions so as to be attenuated rapidly between the first- and second-nearest neighbours in the diamond structure. r_c is the step position and n_c expresses the sharpness of the step. For the parameters, firstly, they used $n = 2$ and determined the coefficients $V_{ll'm}^0$ from Harrison [15]. The other parameters are $m = 4.54$, $r_c = 3.67 \text{ \AA}$, $n_c = 6.48$ and $\varphi(r_0) = 3.4581$. All these parameters were determined so as to reproduce the equilibrium energies, volumes and bulk moduli of diamond and FCC structures of Si [6]; it should be noted that the sp energy splitting ΔE_{sp} was also adjusted for this purpose to be 8.295 eV.

Sawada [11] has proposed a similar method independently. In this method, the two-centre hopping integrals are also expressed using a $1/r^n$ form and an attenuation function $S(r)$ as:

$$V_{ll'm}(r) = \eta_{ll'm} S(r) r^{-\nu} \quad (3)$$

Table 1. The parameter values in the method of Sawada [11]. $\Delta E_{sp} = 4.39$ eV, $\lambda_1 = 1.086 \text{ \AA}^{-2}$, $\lambda_2 = 8.511 \text{ \AA}^{-1}$, $a_0 = 300.2715 \text{ eV \AA}^5$, $a_1 = 4.8227 \text{ eV \AA}^5$. The values of a_0 and a_1 are those readjusted in this letter.

	Hopping integrals				Repulsive potential
	ss σ	sp σ	pp σ	pp π	
ν	4	3	2	2	5
η (eV \AA^ν)	-63.9	27.7	13.1	-2.94	—
μ (\AA^{-1})	5.96	5.96	2.55	2.55	2.55
R_c (\AA)	3.17	3.17	3.83	3.83	3.83

where

$$S(r) = 1/\{1 + \exp[\mu(r - R_c)]\}. \quad (4)$$

The repulsive potential has a similar functional form, but has dependence on the local environment as follows:

$$\varphi(r_{ij}) = A_{ij}S(r_{ij})r_{ij}^{-\nu} \quad (5)$$

where

$$A_{ij} = a_0 - a_1(Z_i + Z_j). \quad (6)$$

Z_i is the effective co-ordination number of the atom i and is given by

$$Z_i = \sum_{j \neq i} \exp[-\lambda_1(r_{ij} - R_i)^2] \quad (7)$$

where

$$R_i = \sum_{j \neq i} r_{ij} e^{-\lambda_2 r_{ij}} \left[\sum_{j \neq i} e^{-\lambda_2 r_{ij}} \right]^{-1}. \quad (8)$$

All the parameters in the method of Sawada are shown in table 1. For the parameters of the two-centre hopping integrals, different exponent values were selected following the work by Robertson [16] and others were determined so as to reproduce the first- and second-neighbour hopping integrals of diamond Si given by Pandey and Phillips [17]. The parameters for the repulsive potential were then determined so as to reproduce the binding energies and equilibrium volumes of various phases of Si including a dimer. The final procedure is the determination of a_0 and a_1 . In the methodology used by Sawada, if the other parameters are selected properly, it is possible that the necessary magnitudes of A_{ij} for respective structures of Si are expressed using a simple functional form of the effective coordination numbers such as equation (6). Of course, other functional forms should be possible for an alternative selection of parameter values.

Using the above two types of transferable SETB method, we have calculated the binding energy–volume curves for six crystal structures of Si: FCC, BCC, SC, β -tin, wurtzite and diamond structures. In view of applying these methods to molecular dynamics, no artificial truncation of the neighbours is used in the present calculations. The axial ratio in the β -tin structure is fixed at 0.5516 and the ideal ratio is used for the wurtzite structure. The band structure energies have been obtained not by the recursion method [10, 11] but by the k space method in order to obtain more accurate results. For integration over the Brillouin zone, the special points [18] have been used in wurtzite and diamond

structures. In the other structures, we have used a simple sampling method of a uniform mesh. Of course, we had to use sufficiently dense meshes. For example, at the equilibrium volume of the sc structure, the difference between the band structure energy obtained with the mesh used and that obtained with the mesh 64 times denser is less than 0.002 eV/atom. The present energy-volume curves obtained by the above two methods are slightly different from the published ones [10, 11]. This may be caused by the artificial truncation of the neighbours used in the published cases, or by the difference in the calculation of the band structure energy.

In the present binding energy-volume curves obtained by the method of Goodwin *et al*, the reproduction of the equilibrium volumes of FCC and BCC structures is indeed much improved as compared with the usual SETB method [8] and the stability of the diamond structure and the high-pressure diamond to β -tin transition are well reproduced. However, if one demands accuracy in a similar range to that achieved with the methods using the recent inter-atomic potentials [3-5], there are some drawbacks. Firstly, all the calculated equilibrium volumes of FCC, BCC, sc and β -tin structures are about 10% larger than the *ab initio* results [6]. Secondly, the equilibrium energy of the FCC structure is lower than that of the BCC structure thus differing from the *ab initio* results. Thirdly, the relative equilibrium energies of the sc and β -tin structures against that of the diamond structure are about 1.6 and 1.7 times larger than the *ab initio* results.

The first point might be improved by selecting other parameter values within the methodology of Goodwin *et al* because the present equilibrium volume of diamond structure is also 6.6% larger than the experimental value. However, the second and third points seem to be difficult to improve simply by 'rescaling' in their methodology because these points are also seen in the usual SETB method [8]. We have tried to improve the above points by adjusting the parameters m and $\varphi(r_0)$. Under the condition of accurate reproduction of the experimental equilibrium volume of diamond structure, selection of values for the pairs of m and $\varphi(r_0)$ is limited. If one does not care about the shift of the absolute values of the binding energies, it is possible to improve the first point, for example, using $m = 4.72$ and $\varphi(r_0) = 3.086$. However, in this case, the second and the third points are not yet improved and the equilibrium energies of the FCC and BCC structures are in a similar range to those of sc and β -tin structures.

An additional most serious drawback in the method and parameters proposed by Goodwin *et al* is that the band structure of diamond Si is reproduced to be semi-metallic. This is caused by the adjusted large value of ΔE_{sp} and the non-zero values of the second-neighbour hopping integrals. This can be understood by analysing the Hamiltonian matrix elements of the diamond structure at the Γ point. Within the second-neighbour expression, there exist only four types of non-zero elements at the Γ point. The condition that the gap is generated at the Γ point is $E_{p'} - E_{s'} < |4E_{ss}| + |4E_{xx}|$, where $E_{s'} = E_s + 12V_{ss\sigma}(2)$, $E_{p'} = E_p + 4V_{pp\sigma}(2) + 8V_{pp\pi}(2)$, $4E_{ss} = 4V_{ss\sigma}(1)$ and $4E_{xx} = 4(1/3V_{pp\sigma}(1) + 2/3V_{pp\pi}(1))$. 1 and 2 in the parentheses indicate the first- and second-neighbour hopping integrals. The value of $|4E_{ss}| + |4E_{xx}|$ is about 9.045 eV in the present case. However, the value of $E_{p'} - E_{s'}$ is 9.075 eV and does not satisfy the above condition. This is caused by the large value of ΔE_{sp} and the non-zero second-neighbour hopping integrals.

We have examined a smaller value of ΔE_{sp} , for example, 6.45 eV, and a proper set of m and $\varphi(r_0)$ that can reproduce the equilibrium volume of diamond structure. However, the relative energies of the FCC, BCC, sc and β -tin structures against the equilibrium binding energy of the diamond structure are reproduced to be 2 or 3 times larger than the *ab initio* results. It seems that the large value of ΔE_{sp} is necessary in

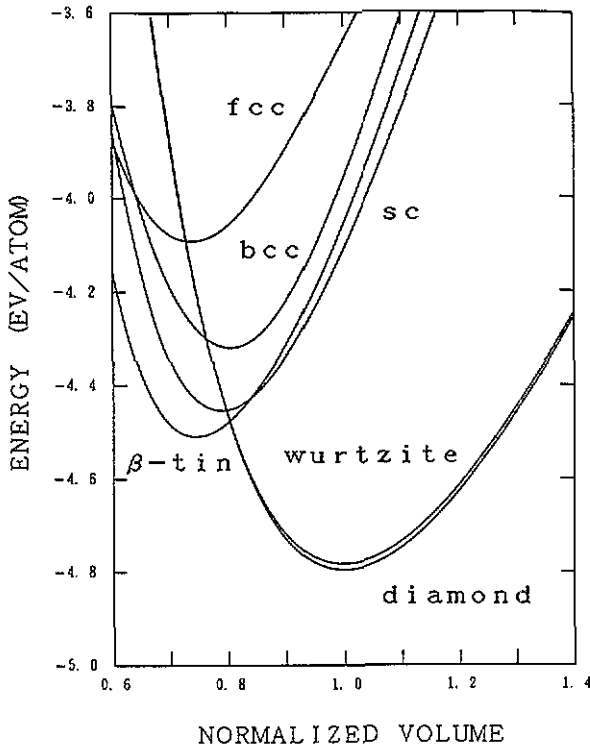


Figure 1. Binding energy-volume curves for six crystal structures of Si calculated using the transferable SETB method proposed by Sawada with the parameters in table 1.

decreasing the relative energies of the close packed structures against the binding energy of the diamond structure in the present method.

Using the method of Sawada, we obtained more satisfactory results. However, in the calculations of Sawada [11], the interactions were truncated after the second neighbours in the FCC, BCC, SC and diamond structures. We have found that this affects the results substantially. Thus, in order to obtain satisfactory results in the present scheme where no truncation of the neighbours is used, we have readjusted only the two parameters, a_0 and a_1 , following the above-mentioned methodology of Sawada. The adjusted parameters are listed in table 1. Figure 1 and table 2 show the present results using the adjusted parameters.

Here, it should be noted that the spin-polarization energy of a free atom is neglected in the Sawada method. However, this is not a serious problem. From the viewpoint of determining the total energies of various systems against that of the perfect crystal of Si, the essential values are the relative binding energies against the equilibrium binding energy of the diamond structure.

As shown in figure 1 and table 2, the observed equilibrium volume of the diamond structure is reproduced exactly. All the equilibrium volumes of various structures are reproduced with errors less than several percent as compared with the *ab initio* results [6]. The relative energies of various structures against the equilibrium binding energy of the diamond structure are also well reproduced. In particular, both the relative

Table 2. Equilibrium volumes and binding energies of six crystal structures of Si calculated using the transferable SETB method proposed by Sawada with the parameters in table 1. V_{min} , E_{min} and ΔE_{min} are the equilibrium volume, the equilibrium binding energy and the relative equilibrium binding energy against that of diamond structure. V_0 is the observed volume of diamond structure. The values in the parentheses are the *ab initio* results [6].

	V_{min}/V_0	E_{min} (eV/atom)	ΔE_{min} (eV/atom)
diamond	1.0 (1.012)	-4.80 (-4.84)	
FCC	0.737 (0.733)	-4.09	0.70 (0.57)
BCC	0.805 (0.736)	-4.32	0.48 (0.53)
sc	0.790 (0.808)	-4.45	0.34 (0.35)
β -tin	0.744 (0.773)	-4.51	0.29 (0.27)
wurtzite	0.999 (1.015)	-4.78	0.013 (0.016)

equilibrium energies and volumes of SC and β -tin structures are very accurately reproduced. The energy of the BCC structure is reproduced to be lower than that of the FCC structure as well as the *ab initio* results. The calculated bulk modulus of the diamond structure is 0.92 Mbar, which is close to the experimental value, 0.99 Mbar. The noticeable drawback is only that the relative equilibrium energy of the FCC structure is overestimated by about 20%. It should be noted that the present results are comparable to the results using the inter-atomic potentials recently proposed [3–5]. Of course, the band structure of diamond Si is similarly well reproduced in comparison with that obtained by Pandey and Phillips [17].

It can be said that the transferable SETB method proposed by Sawada is much superior to the method of Goodwin *et al* in reproducing the binding energy–volume curves of various structures of Si accurately. It is now possible to apply the Sawada method with the parameters adjusted in the present letter to lattice defects or disordered systems of Si where not all the atoms are fourfold-coordinated. We are currently using this scheme in calculations of grain boundaries in Si. The method of Goodwin *et al* has serious drawbacks and it does not seem that all the drawbacks may be overcome within their methodology, as shown above.

The present results indicate the importance of incorporating the dependence on the local environment into the repulsive energy in the transferable SETB method. This point can be explained as follows from the origin of the repulsive energy in the SETB method. With regard to the origin of the repulsive energy, two types of idea have been suggested. The first regards the origin of the repulsive energy as the electrostatic and exchange-correlation interaction. Chadi [7] first proposed that the origin of the repulsive energy is the electrostatic effect, namely, the ion–ion repulsion and the doubly counted electron–electron correction, $E_{i-i} - E_{e-e}$, within the Hartree approximation. Recently, this point of view has been extended and clarified within the density-functional theory [19–21]. Using the stationary approximation to the self-consistent density-functional theory with the superposition of neutral atomic charges as an input density, it has been shown that the energy terms other than the band structure energy, namely, the doubly counted

electron–electron correction, the exchange–correlation correction and the ion–ion repulsion, are well approximated as a simple sum of transferable inter-atomic pairwise repulsive potentials [20, 21].

The second type of idea was proposed by Harrison [12, 13]. He proposed that the origin of the repulsive energy is the overlap interaction, in other words, the non-orthogonality between the local basis orbitals neglected in calculation of the band structure energy with approximate orthogonalization of basis orbitals. Majewski and Vogl [14] have incorporated the overlap matrix to first order into the on-site elements of the Hamiltonian and have shown that the overlap interaction generates repulsive energy. It should be noted that the repulsive energy caused by the overlap interaction cannot be expressed as a simple sum of transferable pairwise potentials in principle, but depends on the local environment.

It can be said that both the two types of idea are right. In other words, both the electrostatic and exchange–correlation interaction and the overlap interaction should be regarded as the origins of the repulsive energy in the SETB method. Recently, this has been shown using the chemical pseudopotential theory [22] and it seems that the overlap interaction is more important with respect to the transferability in the SETB method. This is the reason the incorporation of the dependence on the local environment into the repulsive energy is important in the present transferable SETB method. Within the first type of idea shown in [20] and [21], it seems possible to approximate the repulsive energy as a simple sum of transferable pairwise repulsive potentials, as in the method of Goodwin *et al.* However, it should be noted that the overlap interaction is already incorporated into the band structure energy in [20] and [21], where the non-orthogonality of basis orbitals is dealt with correctly. In the case of the SETB method using approximate orthogonality of basis orbitals where the overlap interaction is not directly incorporated into the band structure energy, it is necessary to incorporate the effect of the overlap interaction into the repulsive energy in addition to the pairwise repulsion based on the electrostatic and exchange–correlation interaction.

Of course, the method of Sawada itself is not intended for incorporating the above mentioned effect directly into the form of repulsive energy but is a more phenomenological case and there are other types of SETB method incorporating the dependence on the environment into the repulsive energy through the number of bonds [23, 24]. However, at present, it seems that the method of Sawada is excellent at least in representing the binding energies and equilibrium volumes of various coordinated structures of Si.

Finally, it should be noted that incorporating the overlap effect directly into the electronic structure calculation is important with respect to the transferability in the electronic structure calculation as pointed out in [25]. It has been shown that this type of transferability is possible in the non-orthogonal tight-binding (NTB) method [26]. With respect to this point, it has been found that the band structures other than those of fourfold-coordinated structures are not necessarily well reproduced in the present method of Sawada as compared with the results in [26] because the overlap effect is not included in the electronic structure calculation itself. Therefore, in order to develop the methods with better transferability in representing not only total energy but also electronic structure in future, it might be more effective to reform or supplement such methods as the NTB method [26] or the SCTB method [9,14], where the overlap effect is incorporated in the electronic structure calculation.

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