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The self-consistent tight-binding method: application to silicon and silicon carbide

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Abstract. The self-consistent tight-binding (SCTB) model proposed by Majewski and Vogl has been extended to be applicable for calculations of lattice defects in solids or disordered systems with both ionic and covalent characters that cannot be treated using other types of tight-binding theories. The precise formulation of electronic structure, total energy and atomic forces in the supercell technique has been presented. In order to apply this method to lattice defects in SiC, the parameters and functional forms have been examined so as to reproduce the basic properties of Si, SiC and C. The nature of the bonding and the phase stability in Si and SiC have been analysed by the present SCTB method.

1. Introduction

By virtue of the advances in theoretical methods in solid-state physics and the development of high-performance computers, it is possible to investigate theoretically the atomic structures and total energies of complex systems, such as dislocations, surfaces, grain boundaries, amorphous systems, liquids or clusters. The theoretical methods can be classified into the following three groups.

The first group is the *ab initio* method, where atomic structures and total energies are determined via first-principles calculations of electronic structures. The recent development of the dynamical simulated annealing method [1] has enabled us to deal with systems of a large number of atoms from the first-principles density-functional theory. However, this type of method is time-consuming as yet, and the numbers of tractable atoms are limited as compared with the other groups of methods.

The second group is empirical methods where atoms or ions are treated without calculating electronic structures. For ionic solids or metals, total energies are frequently expressed as a sum of two-body inter-ionic or inter-atomic potentials [2, 3]. Recently, for covalent solids such as Si, various inter-atomic potentials including many-body terms have been proposed [4]. In these methods, calculations of total energies and atomic forces are quite simple, and a fairly large number of atoms can be dealt with. However, inter-ionic or inter-atomic potentials are determined empirically in general, and results should be regarded as qualitative. It should be noted that it is not possible to determine simple potential forms between atoms applicable to any local environments, especially in covalent systems, where it is essential to calculate electronic structure.

The third group of theoretical methods are those where total energies and atomic forces are given via semi-empirical calculations of electronic structures. These methods intervene between the former two groups of theoretical schemes. The quantitative reliability is not necessarily enough as compared with the *ab initio* methods, but a fairly large number of atoms can be dealt with by virtue of simple expressions of electronic structures and total energies. For example, the semi-empirical tight-binding (SETB) method [5] and the tight-binding bond (TBB) model [6] have been shown to be quite useful for calculations of various systems of semiconductors and transition metals [7–9]. In these methods, total energies are expressed as a sum of the band-structure energy and the short-range repulsive interaction between atoms. The band-structure energy is a sum of occupied eigenenergies calculated via the tight-binding approximation [10]. The atomic forces can be given quite simply via the Hellmann–Feynman theorem [5, 6, 11].

It should be noted that the SETB method and the TBB model are effective in semiconductors or transition metals, where the inter-atomic electrostatic interaction can be neglected or local charge neutrality is a good approximation. Recently, attempts to justify these semi-empirical schemes from the first-principles density-functional theory have been carried out [6, 12], where it is essential that the self-consistent charge distribution is not too different from the superposition of free atomic charges. In other words, the usual tight-binding methods are improper in treating systems with both ionic and covalent characters where charge redistribution and long-range Coulomb interaction are important as well as covalent energy. It is necessary to develop theoretical schemes belonging to the third group and capable of treating systems of both ionic and covalent characters.

The self-consistent tight-binding (SCTB) method [13, 14] is just such a method that belongs to the third group and can deal with both ionicity and covalency on an equal footing. Majewski and Vogl [13] have presented the formulation of calculations of electronic structure and total energy in this method, and have shown that structural properties and crystal stability of various sp-bonded semiconductors and insulators can be adequately reproduced by this method. It is important to apply this method to calculations of lattice defects or disordered systems as well as the SETB method and the TBB model. For this purpose, it is essential to clarify how to calculate atomic forces in this theoretical scheme. In our previous paper [14], we have shown that atomic forces can be given very easily via the Hellmann–Feynman theorem in the SCTB method as well as in other tight-binding theories.

In the present paper, first, we present more clearly the formulation of electronic structure, total energy and atomic forces in periodic systems in order to apply the SCTB method to defect calculations with use of the supercell technique. Secondly, we examine several functional forms and parameters in the SCTB method so as to reproduce the basic properties of Si, SiC and C in order to apply this method to calculation of a grain boundary in SiC in our following paper.

2. Theoretical method

In this section, we formulate the SCTB method for calculating electronic structures, total energies and atomic forces in periodic systems such as supercells or perfect crystals.

The orthogonalised basis functions are constructed as

$$|i\alpha, \boldsymbol{k}\rangle = N^{-1/2} \sum_{\boldsymbol{R}} \exp[\mathrm{i}\boldsymbol{k} \cdot (\boldsymbol{t}_i + \boldsymbol{R})]\varphi_{i\alpha}(\boldsymbol{r} - \boldsymbol{t}_i - \boldsymbol{R}) \tag{1}$$

where $\varphi_{i\alpha}(\boldsymbol{r} - \boldsymbol{t}_i - \boldsymbol{R})$ is the αth atomic orbital centred on an atom i located at $\boldsymbol{t}_i + \boldsymbol{R}$, $\boldsymbol{R}$ is a lattice vector representing each unit cell of the periodic system and N is the number of unit cells in the system. The eigenfunction with wavevector $\boldsymbol{k}$ and band index n is expressed as

$$|n, \boldsymbol{k}\rangle = \sum_{i\alpha} C_{i\alpha}^{n\boldsymbol{k}} |i\alpha, \boldsymbol{k}\rangle. \tag{2}$$

The Hamiltonian is expressed as

$$\begin{aligned}\mathcal{H} = {} & \sum_{\boldsymbol{R}} \sum_{i\alpha} |\varphi_{i\alpha}(\boldsymbol{r} - \boldsymbol{t}_i - \boldsymbol{R})\rangle E_{i\alpha} \langle \varphi_{i\alpha}(\boldsymbol{r} - \boldsymbol{t}_i - \boldsymbol{R})| \\ & + \sum_{\boldsymbol{R}} \sum_{\boldsymbol{R}'} \sum_{i\alpha} \sum_{j\beta} |\varphi_{i\alpha}(\boldsymbol{r} - \boldsymbol{t}_i - \boldsymbol{R})\rangle H_{\alpha\beta}(\boldsymbol{t}_i + \boldsymbol{R}, \boldsymbol{t}_j + \boldsymbol{R}') \\ & \times \langle \varphi_{j\beta}(\boldsymbol{r} - \boldsymbol{t}_j - \boldsymbol{R}')|. \end{aligned} \tag{3}$$

Here $H_{\alpha\beta}(\boldsymbol{t}_i + \boldsymbol{R}, \boldsymbol{t}_j + \boldsymbol{R}')$ is the Hamiltonian matrix element between the two atomic orbitals and is expressed using the two-centre integrals via the two-centre approximation [10].

In equation (3) $E_{i\alpha}$ is the on-site element. In the SCTB method, the effects of the charge transfer between atoms and the overlap between atomic orbitals are included in this on-site element self-consistently as follows:

$$E_{i\alpha} = E_{i\alpha}^0 + U_i(Q_i - Z_i) + P_i + f_{i\alpha}. \tag{4}$$

Here $E_{i\alpha}^0$ is the αth energy level of a free atom i. The second term expresses the change in the intra-atomic Coulomb potential. Q_i is the self-consistent occupancy of the atom i, Z_i is the charge of the ion i and U_i is an average of the intra-atomic two-electron Coulomb integrals of the valence electrons in the free atom i. The atomic occupancy is given by the orbital occupancies $Q_{i\alpha}$ as

$$Q_i = \sum_{\alpha} Q_{i\alpha}$$

and

$$Q_{i\alpha} = \sum_{n,\boldsymbol{k}}^{\mathrm{occ}} C_{i\alpha}^{n\boldsymbol{k}*} C_{i\alpha}^{n\boldsymbol{k}} \tag{5}$$

where the sum is taken over occupied eigenstates with wavevector $\boldsymbol{k}$ and band index n.

The third term in equation (4) is the inter-atomic electrostatic potential for an electron located on the atom i and expressed as

$$P_i = (Q_i - Z_i)\Phi_0 + \sum_{j \neq i} (Q_j - Z_j)\Phi_{ij} \tag{6}$$

where

$$\Phi_0 = \sum_{\boldsymbol{R} \neq 0} V(\boldsymbol{R}) \qquad \Phi_{ij} = \sum_{\boldsymbol{R}} V(\boldsymbol{t}_j + \boldsymbol{R} - \boldsymbol{t}_i)$$

and j indicates the atoms other than i in the unit cell. Here $V(\boldsymbol{r}_j - \boldsymbol{r}_i)$ is an effective inter-atomic electrostatic function, which includes the effect of charge overlap for short distances and expresses an ordinary Coulomb interaction for large distances.

The fourth term in equation (4) is the non-orthogonality correction. When the local basis functions are orthogonalised, the effect of the overlap between local atomic orbitals is approximately introduced to first order into the on-site elements [15]. This term is expressed as

$$f_{i\alpha} = -\sum_{j\beta} S_{i\alpha j\beta} H_{j\beta i\alpha}. \tag{7}$$

In this expression, the sum is taken over neighbouring atomic orbitals.

The electronic structure can be given by solving the above one-electron Schrödinger equation self-consistently. The total energy is given within the Hartree approximation as

$$E_{\mathrm{tot}} = E_{\mathrm{bs}} - E_{\mathrm{e\text{-}e}} + E_{\mathrm{i\text{-}i}} \tag{8a}$$

where E_{bs} is the band-structure energy and expressed as

$$E_{\mathrm{bs}} = \sum_{n,k}^{\mathrm{occ}} E_{nk} = \sum_{i\alpha} Q_{i\alpha} E_{i\alpha} + \sum_{n,k}^{\mathrm{occ}} \sum_{i\alpha} \sum_{j\beta} C_{i\alpha}^{nk*} C_{j\beta}^{nk} \sum_{\boldsymbol{R}} \exp[\mathrm{i}\boldsymbol{k} \cdot (\boldsymbol{t}_j + \boldsymbol{R} - \boldsymbol{t}_i)] H_{\alpha\beta}(\boldsymbol{t}_i, \boldsymbol{t}_j + \boldsymbol{R}) \tag{8b}$$

and E_{nk} is the eigenenergy. The binding energy E_{B} is defined as $E_{\mathrm{tot}} - E_{\mathrm{atom}}^0$, where E_{atom}^0 is the total energy of the free atoms constituting the system. As shown in our previous paper [14], the binding energy per unit cell in the periodic system can be expressed as a sum of the following four terms:

$$E_{\mathrm{B}} = E_{\mathrm{pro}} + E_{\mathrm{cov}} + E_{\mathrm{ov}} + E_{\mathrm{Mad}} \tag{9a}$$

where

$$E_{\mathrm{pro}} = \sum_i \left(\sum_\alpha Q_{i\alpha}(E_{i\alpha}^0 - U_i Z_i) + \tfrac{1}{2} U_i Q_i^2 \right) - E_{\mathrm{atom}}^0 \tag{9b}$$

$$E_{\mathrm{cov}} = E_{\mathrm{bs}} - \sum_{i\alpha} Q_{i\alpha} E_{i\alpha} = \sum_{n,k}^{\mathrm{occ}} \sum_{i\alpha} \sum_{j\beta} C_{i\alpha}^{nk*} C_{j\beta}^{nk} \times \sum_{\boldsymbol{R}} \exp[\mathrm{i}\, \boldsymbol{k} \cdot (\boldsymbol{t}_j + \boldsymbol{R} - \boldsymbol{t}_i)] H_{\alpha\beta}(\boldsymbol{t}_i, \boldsymbol{t}_j + \boldsymbol{R}) \tag{9c}$$

$$E_{\mathrm{ov}} = \sum_{i\alpha} Q_{i\alpha} f_{i\alpha} \tag{9d}$$

and

$$E_{\mathrm{Mad}} = \tfrac{1}{2} \sum_i (Q_i - Z_i)^2 \Phi_0 + \tfrac{1}{2} \sum_i \sum_{j \neq i} (Q_i - Z_i)(Q_j - Z_j) \Phi_{ij}. \tag{9e}$$

E_{pro} includes the promotion energy and the change in the intra-atomic electrostatic energy. E_{cov} is the covalent energy. This term is given by subtracting the on-site contributions from the band-structure energy, and contains only the contributions from the inter-atomic covalent bonding. E_{ov} is the overlap interaction energy, which expresses the increase in the kinetic energy of the electrons upon compression [15, 16]. This term is often given by a simple sum of inter-atomic potentials in usual tight-binding theories. In the present formulation, the effect of local electronic structure can be incorporated

in this term. E_{Mad} is the inter-atomic electrostatic interaction energy, which is a sum of the interactions between atoms with effective charges, $Q_i - Z_i$.

As shown in our previous paper [14], the atomic forces in the SCTB method can also be given very easily via the Hellmann–Feynman theorem. This is applicable also in the periodic system as follows:

$$-\boldsymbol{F}_l = \frac{\partial E_{\mathrm{tot}}}{\partial \boldsymbol{t}_l} = \sum_{n,k}^{\mathrm{occ}} \sum_{i\alpha} \sum_{j\beta} C_{i\alpha}^{nk*} C_{j\beta}^{nk} \sum_{\boldsymbol{R}} \exp[\mathrm{i}\boldsymbol{k} \cdot (\boldsymbol{t}_j + \boldsymbol{R} - \boldsymbol{t}_i)]$$
$$\times \frac{\partial}{\partial \boldsymbol{t}_l} \boldsymbol{H}_{\alpha\beta}(\boldsymbol{t}_i, \boldsymbol{t}_j + \boldsymbol{R}) + \sum_{i\alpha} Q_{i\alpha} \frac{\partial f_{i\alpha}}{\partial \boldsymbol{t}_l} + \tfrac{1}{2} \sum_i \sum_{j \neq i} (\boldsymbol{Q}_i - \boldsymbol{Z}_i)(\boldsymbol{Q}_j - \boldsymbol{Z}_j) \frac{\partial \Phi_{ij}}{\partial \boldsymbol{t}_l}. \quad (10)$$

The atomic forces are given only by solving the Schrödinger equation self-consistently. The first term is the contribution from the covalent energy. This is essentially a many-body force given by the electronic structure of the system. The second term is the contribution from the overlap interaction. The third term is the contribution from the inter-atomic electrostatic interaction.

It should be noted that in the present SCTB method both covalency and ionicity can be treated on an equal footing. In the SETB method [5], the self-consistency and the inter-atomic electrostatic interaction energy E_{Mad} are neglected in general. In the TBB model [6], the local charge neutrality is imposed and E_{Mad} is forced to be zero. It is obvious that these two methods are not capable of treating systems where both covalent and ionic characters are important. On the other hand, the ionic model [2], where the total energy is expressed as a sum of inter-ionic electrostatic potentials, corresponds to the neglect of E_{cov} in the total energy. This model is also improper in a system containing covalency.

In this way, the remaining work is to determine the functional forms and parameters for the two-centre integrals of the Hamiltonian and the overlap matrix, the effective inter-atomic electrostatic function and so on. If this work can be done successfully, the SCTB method with the above-mentioned formulation is a powerful scheme for calculations of lattice defects or disordered systems with both ionic and covalent characters as well as the SETB method and the TBB model in covalent systems. Fortunately, Majewski and Vogl [13] have found that simple and universal functional forms and parameters can be applicable to various sp-bonded semiconductors and insulators.

In the next section, in order to apply the SCTB method to lattice defects in SiC, we have examined several sets of functional forms and parameters so as to reproduce the basic properties of Si, SiC and C. In the lattice defects such as grain boundaries in SiC, it is possible that there exist Si–Si or C–C bonds. Thus it is necessary that the basic properties of all Si, SiC and C are reproduced by using the SCTB method. Unfortunately, this is not so easy because elements and compounds with atoms in the first row of the periodic table have special characters in general.

3. Functional forms and parameters for Si, SiC and C

3.1. Functional forms and parameters of Majewski and Vogl

Majewski and Vogl [13] have shown that structural properties and crystal stability of various sp-bonded semiconductors and insulators can be adequately reproduced by the SCTB method using the following functional forms and parameters. We first of all apply these forms and parameters to Si, SiC and C.

Table 1. Atomic term values, intra-atomic Coulomb repulsion and universal tight-binding parameters [13]†.

	Si	C
E_s^0 (eV)	−14.68	−19.19
E_p^0 (eV)	−8.08	−11.79
U (eV)	7.64	11.76
$\eta_{ss\sigma} = -1.38$	$\eta_{sapc\sigma} = 1.68$	$\eta_{scpa\sigma} = 1.92$
$\eta_{pp\sigma} = 2.20$	$\eta_{pp\pi} = -0.55$	

† In the η parameters, a and c denote anion and cation. For elemental solids, the average is taken.

The basic functions are constructed by one s and three p valence atomic orbitals per atom. The two-centre integrals of the Hamiltonian are expressed by assuming the r^{-2} dependence on the inter-atomic distance r [5, 15] as

$$H_{ll'm} = \eta_{ll'm}\hbar^2/mr^2. \tag{11}$$

The parameters $\eta_{ll'm}$ for nearest neighbours are given in table 1. These were fitted to obtain adequate band structures for various semiconductors [17]. We have used these common parameters for Si, SiC and C. The coupling of second-nearest neighbours can be neglected as discussed in [13]. The energy levels of the free atoms and the intra-atomic Coulomb repulsion in equation (4) are also listed in table 1. The former were taken from those by the Hartree–Fock calculations [18] and the latter were determined by Harrison [19].

For the effective inter-atomic electrostatic function $V(\boldsymbol{r}_j - \boldsymbol{r}_i)$ in equation (6), Majewski and Vogl have used the following form [20]:

$$V(\boldsymbol{r}_j - \boldsymbol{r}_i) = \frac{e^2}{|\boldsymbol{r}_j - \boldsymbol{r}_i|} - \frac{e^2}{|\boldsymbol{r}_j - \boldsymbol{r}_i|}\exp\left(-\frac{U_a + U_c}{2}\frac{|\boldsymbol{r}_j - \boldsymbol{r}_i|}{e^2}\right). \tag{12}$$

Here U_a and U_c are the intra-atomic Coulomb repulsion of anion and cation. This function represents the simple Coulomb function for large distances and expresses the effect of charge overlap for short distances. In order to apply this functional form in general periodic systems, it is necessary to use the method of summation in reciprocal space, such as the Ewald method [21], because the sum of the first term of equation (12) does not converge in real space differently from the sum of the second term of equation (12). This method is familiar in calculations of ionic systems [2] and the contributions from the first term of equation (12) in Φ_0 and Φ_{ij} of equation (6) can be given as

$$\Phi_0^{\mathrm{Ew}} = e^2 \sum_{\boldsymbol{R}\neq 0} \frac{1}{|\boldsymbol{R}|}$$

$$= e^2\left(\frac{\pi}{v_c}\frac{1}{\gamma^2}\sum_{G\neq 0}\frac{\exp(-G^2/4\gamma^2)}{G^2/4\gamma^2} + \sum_{\boldsymbol{R}\neq 0}\frac{1}{|\boldsymbol{R}|}\operatorname{erfc}(|\boldsymbol{R}|\gamma) - \frac{2\gamma}{\pi^{1/2}}\right) \tag{13a}$$

$$\Phi_{ij}^{\mathrm{EW}} = e^2\sum_{\boldsymbol{R}}\frac{1}{|\boldsymbol{t}_j + \boldsymbol{R} - \boldsymbol{t}_i|} = e^2\left(\frac{\pi}{v_c}\frac{1}{\gamma^2}\sum_{G\neq 0}\frac{\exp(-G^2/4\gamma^2)}{G^2/4\gamma^2}\exp[\mathrm{i}\boldsymbol{G}\cdot(\boldsymbol{t}_j - \boldsymbol{t}_i)]\right.$$

Table 2. Results using a $1/r^3$ form for overlap integrals†.

	Si	SiC	C
K	1.1507	1.4673	1.7637
E_{pro} (eV/cell)	9.59	12.85	15.19
E_{cov} (eV/cell)	−37.33	−59.72	−91.09
E_{ov} (eV/cell)	14.93	23.98	36.44
E_{Mad} (eV/cell)	—	−1.47	—
E_B (eV/cell)	−12.81	−24.36	−36.47
	(−9.26)	(−12.68)	(−14.74)
B (Mbar)	0.88	2.90	8.24
	(0.99)	(2.24)	(4.43)
Effective charge	—	0.4498e	—

† Values in parentheses are the experimental ones.

$$+\sum_{R} \frac{1}{|\boldsymbol{R}+\boldsymbol{t}_j-\boldsymbol{t}_i|} \operatorname{erfc}(|\boldsymbol{R}+\boldsymbol{t}_j-\boldsymbol{t}_i|\gamma)\Big) \tag{13b}$$

where γ is a parameter selected for rapid conversion and v_c is the volume of the unit cell. Here $\{\boldsymbol{G}\}$ are the reciprocal lattice vectors defined by the lattice vectors $\{\boldsymbol{R}\}$ of the periodic system. The derivative of equation (13*b*) used in equation (10) can be calculated using a similar formula. For SiC in the zincblende structure, we found that the sums with respect to $\{\boldsymbol{G}\}$ in equations (13*a*) and (13*b*) converge for $|\boldsymbol{G}| > 20$ Å^{-1} and those with respect to $\{\boldsymbol{R}\}$ converge for $|\boldsymbol{R}| > 10$ Å. Also we found that the sum of the second term of equation (12) converges for distances larger than 60 Å.

The overlap matrix elements in equation (7) are simplified by the two-centre approximation as well as the Hamiltonian. The determination of the functional form of the two-centre overlap integrals $S_{ll'm}$ is important because the repulsive interaction between atoms is determined by this functional form. As well as Harrison [22], Majewski and Vogl [13] have proposed a functional form following extended Hückel theory [23]. This is not a $1/r^2$ form [22] but a $1/r^3$ form:

$$S_{ll'm} = \eta_{ll'm}[2/(E^0_{il} + E^0_{jl'})](\hbar^2/m)(d_0/Kr^3) \tag{14}$$

where $d_0 = e^2(1/U_i + 1/U_j)/2$. Majewski and Vogl have determined the parameter K for each row of the periodic table to obtain adequate overall agreement with the experimental bond length and bulk modulus of various sp-bonded semiconductors and insulators. In this paper, we have determined K for Si, SiC and C, respectively, so as to reproduce the experimental bond length.

In this way, we have calculated several basic properties of Si, SiC and C using the above-mentioned functional forms and parameters. The $\boldsymbol{k}$ sums were performed using 60 special $\boldsymbol{k}$-points [24]. In table 2, the fitted parameters K and the calculated energy values and bulk moduli B are shown. E_B is $E_{tot} - E^0_{atom}$, and is equal to the negative of the cohesive energy E_{coh}. E^0_{atom} contains the spin-polarised energies. The values of K in [13] are 1.31 for Si and 1.67 for C. The calculated effective charge of atoms in SiC is comparable with the effective charge 0.41e determined experimentally [25]. This charge transfer is caused by the difference in the on-site energies.

For Si, E_B and B are adequately reproduced. However, for SiC and C, E_B and B are much overestimated. Especially, the calculated values of E_B are 1.9 times and 2.7 times

Table 3. Results using a $1/r^2$ form for overlap integrals†.

	Si	SiC	C
K	0.6074	0.9144	1.4502
E_{pro} (eV/cell)	9.70	12.98	15.35
E_{cov} (eV/cell)	−37.43	−59.83	−91.22
E_{ov} (eV/cell)	18.71	30.03	45.61
E_{Mad} (eV/cell)	—	−1.46	—
E_B (eV/cell)	−9.02	−18.29	−30.26
	(−9.26)	(−12.68)	(−14.74)
B (Mbar)	0.55	1.89	5.42
	(0.99)	(2.24)	(4.43)
Effective charge	—	0.4483e	—

† Values in parentheses are the experimental ones.

larger in magnitude than the experimental values for SiC and C, respectively. Also the thermodynamic stability condition of SiC, $E_{coh}(\mathrm{SiC}) > [E_{coh}(\mathrm{Si}) + E_{coh}(\mathrm{C})]/2$, is not satisfied. This condition is important in calculations of defects in SiC containing Si–Si and C–C bonds.

Similar overestimation of the binding energy has been reported by Majewski and Vogl [13] for compounds of short bond lengths such as BeO. As pointed out by Harrison [22], it seems that the most important thing is the approximate manner in which the overlap integrals are treated. Thus we examine other functional forms and parameters for $S_{ll'm}$ in equation (14).

3.2. *Use of a $1/r^n$ form for overlap integrals*

We have examined a $1/r^2$ form for overlap integrals following Harrison [22] instead of the above $1/r^3$ form. We have replaced d_0/r^3K in equation (14) by $1/r^2K$ and have fitted K so as to reproduce the experimental bond lengths. The fitted parameters and the calculated energy values and bulk moduli are listed in table 3.

With respect to the energy terms, the change of the form of $S_{ll'm}$ has mainly affected the overlap energies E_{ov}. The other terms are not so different from those in table 2. This is because the change in $f_{i\alpha}$ results in the overall shift of all the on-site elements $E_{i\alpha}$ of the Hamiltonian and does not affect the electronic structure itself so much. As shown in table 3, E_{ov} has been raised and the overestimation of the binding energies of SiC and C is somewhat improved. For Si, the reproduction of E_B is quite good. With respect to the bulk modulus B, values for SiC and C have been improved, although that for Si has been reduced too much. It should be noted that the thermodynamic stability condition of SiC is not yet satisfied.

If $S_{ll'm}$ is a $1/r^n$ form in general, it is possible to analyse calculated values of E_B and B in simple representation [26]. Suppose that E_B is expressed as a function of a bond length r. E_{cov} and E_{ov} directly depend on r, although the dependence of the other terms on r is indirect and weak. From the viewpoint of the bond orbital model [15], where the integration over the eigenstates in the Brillouin zone is replaced by a sum over the bond orbitals, the part of E_B directly dependent on r is expressed as a sum of the bond energy $E_{bond}(r)$, which is $E_{cov}(r) + E_{ov}(r)$ for respective bonds. $E_{cov}(r)$ and $E_{ov}(r)$ are simplified as $-\alpha/r^2$ and β/r^{n+2}, respectively, because of the r^{-2} dependence of $H_{ll'm}$ and the r^{-n}

dependence of $S_{ll'm}$. In the present case, α is common in Si, SiC and C. By the condition of the reproduction of the experimental bond length r_0, β is expressed using r_0 and α. Therefore,

$$E_{\text{bond}}(r_0) = -\alpha/r_0^2 + [2/(n+2)](\alpha/r_0^2) = -[n/(n+2)](\alpha/r_0^2). \tag{15}$$

The bulk modulus is also expressed as

$$B = (1/4\sqrt{3})2n(\alpha/r_0^5) \tag{16}$$

and $1/4\sqrt{3}$ is a coefficient in the case that E_{bond} is the energy per bond.

By substituting 3 and 2 for n in equations (15) and (16), it can be found that the calculated values in tables 2 and 3 obey these equations well. The calculated values of $E_{\text{cov}}(r_0)$ and $E_{\text{ov}}(r_0)$ respectively have overall inverse-square dependence on the bond lengths r_0 of Si, SiC and C. The ratio of $E_{\text{ov}}(r_0)$ to $E_{\text{cov}}(r_0)$ is about $-2/5$ and about $-1/2$ in tables 2 and 3, respectively, as predicted by equation (15). The calculated values of B for Si, SiC and C have roughly inverse-fifth dependence on the bond lengths, and the ratio of the values in table 2 to those in table 3 is roughly 3/2 as predicted by equation (16).

From the analysis of equations (15) and (16), it can be said that the calculated $E_{\text{bond}}(r_0)$ of Si, SiC and C should have general inverse-square dependence on the bond lengths r_0 (1:1.6:2.3) and that the calculated B should have general inverse-fifth dependence on the bond lengths (1:3.0:8.2) for any value of n. However, the ratio between the experimental values of $E_{\text{B}}(r_0) = -E_{\text{coh}}$ of Si, SiC and C is about 1:1.4:1.6, and that of B is about 1:2.3:4.5. Therefore, within the present theoretical scheme, it is difficult to find the universal $1/r^n$ form of $S_{ll'm}$ which can adequately reproduce all the experimental values of E_{B} and B for Si, SiC and C.

3.3. Use of a $p/r^m + q/r^n$ form for overlap integrals

The $1/r^3$ or $1/r^2$ forms of $S_{ll'm}$ themselves should be useful for calculations of Si, SiC and C, respectively. However, for the system of SiC containing Si–Si or C–C bonds as shown in our following paper, it is necessary that the basic properties of all Si, SiC and C, at least the stability condition of SiC, should be reproduced. Therefore, in this section, we perform a more empirical approach. We have examined $p/r^m + q/r^n$ forms, where two parameters p and q are fitted so as to reproduce not only the experimental bond length but also the experimental binding energy. Here m and n are integers for simplicity.

When d_0/Kr^3 in equation (14) is replaced by $p/r^m + q/r^n$ with $p, q > 0$ and $m > n \geqslant 0$, calculated values can be predicted as well as the above-mentioned analysis. The bond energy $E_{\text{bond}}(r)$ is simplified as $-\alpha/r^2 + \beta/r^{m+2} + \gamma/r^{n+2}$, where $\alpha, \beta, \gamma > 0$. Here β and γ are determined so as to reproduce the bond length and the binding energy. It can be considered that the energy terms other than $E_{\text{ov}}(r)$ do not depend so much on the shape of $S_{ll'm}$. Thus the fitting for the experimental E_{B} means the fitting of $E_{\text{ov}}(r_0)$ for the value $E_{\text{ov}}^{\text{exp}}$, which is given by subtracting calculated E_{pro}, M_{Mad} and E_{cov} from the experimental E_{B}. Finally, β and γ are expressed using m, n, α, r_0 and $E_{\text{ov}}^{\text{exp}}$, and the bulk modulus B is expressed as

$$B = (1/4\sqrt{3})[(m+2)(n+2)(1 + E_{\text{ov}}^{\text{exp}}/E_{\text{cov}}(r_0)) - mn]\alpha/r_0^5 \tag{17}$$

where $E_{\text{cov}}(r_0)$ is $-\alpha/r_0^2$. The values of $E_{\text{ov}}^{\text{exp}}/E_{\text{cov}}(r_0)$ for Si, SiC and C do not depend so much on the shape of $S_{ll'm}$ and are estimated by the values in tables 2 and 3. Using these values, m and n can be determined so as to reproduce adequately all the experimental

Table 4. Results using a $p/r^4 + q$ form for overlap integrals†.

	Si	SiC	C
p (Å^2)	0.6883	0.4244	0.2988
q (Å^{-2})	0.0214	0.0635	0.1586
E_{pro} (eV/cell)	9.69	13.09	15.63
E_{cov} (eV/cell)	−37.42	−59.93	−91.41
E_{ov} (eV/cell)	18.47	35.61	61.04
E_{Mad} (eV/cell)	—	−1.45	—
E_B (eV/cell)	−9.26	−12.68	−14.74
	(−9.26)	(−12.68)	(−14.74)
B (Mbar)	0.89	2.36	5.45
	(0.99)	(2.24)	(4.43)
Effective charge	—	0.4469e	—

† Values in parentheses are the experimental ones.

values of B for Si, SiC and C. Using the condition $\beta, \gamma > 0$ and comparing the values estimated by equation (16) with the experimental values, it can be concluded that the set $m = 4$ and $n = 0$ is the best choice. The repulsive potential form proposed by Bechstedt and Harrison [27] corresponds to the set $m = 10$ and $n = 1$, although they fitted parameters so as to reproduce the bond length and the bulk modulus. This set should result in overestimation of B in Si and underestimation of B in C in our theoretical scheme.

Table 4 shows the fitted parameters and calculated values by using a $p/r^4 + q$ form for $S_{ll'm}$. As mentioned above, mainly E_{ov} is changed so as to reproduce the experimental E_B. The values of B are adequately reproduced for all Si, SiC and C as compared with the values in tables 2 and 3.

Table 5 shows the summary of the calculated values of E_B and B using the $1/r^3$, $1/r^2$ and $p/r^4 + q$ forms of overlap integrals. The results by a $p\exp(-qr)$ form are also shown. In the calculation using the $p\exp(-qr)$ form, parameters p and q were fitted so as to reproduce the bond length and the binding energy. However, the bulk moduli are poorly reproduced. The calculated phonon frequencies and s–p mixing are also shown. The s–p mixing [28] is the ratio of the p-orbital occupancy to the s-orbital occupancy. These values are comparable with those in [28, 29]. In the calculation of the phonon frequencies, the calculation of atomic forces described in section 2 is utilised. The results of E_B and B for Si agree qualitatively with those by Paxton and Sutton [29]. Our results using the $1/r^3$ form and the $1/r^2$ form for $S_{ll'm}$ correspond to their results using the $1/r^5$ form and the $1/r^4$ form for the inter-atomic repulsive potential, respectively.

It can be said that the $1/r^2$ form of $S_{ll'm}$ is suitable for calculations of structural properties of SiC and C and it seems that the $1/r^3$ form of $S_{ll'm}$ is suitable for Si. It can be said that the $p/r^4 + q$ form is more useful for representing structural properties of all Si, SiC and C. Of course, the stability condition of SiC for Si and C is satisfied in this form.

4. Structural stability

In this section, we report the results on the nature of bonding and the structural stability in Si and SiC calculated using the SCTB method with the above-mentioned functional

Table 5. Summary of binding energies, bulk moduli and phonon frequencies of Si, SiC and C calculated by the SCTB method with several forms of overlap integrals†.

	Si	SiC	C
E_B (eV/cell)			
$1/r^3$	−12.81	−24.36	−39.47
$1/r^2$	−9.02	−18.29	−30.26
p/r^4+q	−9.26	−12.68	−14.74
$p\exp(-qr)$	−9.26	−12.68	−14.74
	(−9.26)	(−12.68)	(−14.74)
B (Mbar)			
$1/r^3$	0.88	2.90	8.24
$1/r^2$	0.55	1.89	5.42
p/r^4+q	0.89	2.36	5.45
$p\exp(-qr)$	0.40	0.84	1.36
	(0.99)	(2.24)	(4.43)
TO(Γ) (THz)			
$1/r^3$	16.9	33.8	60.3
p/r^4+q	17.0	31.1	50.9
	(15.5)	(23.9)	(39.2)
s–p mixing			
$1/r^3$	1.872	2.194	2.439
$1/r^2$	1.888	2.219	2.472
p/r^4+q	1.887	2.243	2.529

† Values in parentheses are the experimental ones.

forms and parameters. Figure 1 shows the dependence on volume of the individual contributions to the binding energy of Si and SiC calculated using the p/r^4+q form for $S_{ll'm}$. The curves for C are qualitatively similar to those for Si. We have examined similar curves using the $1/r^3$ form and the $1/r^2$ form for $S_{ll'm}$. In figure 1, mainly the curves of E_{ov} are changed so as to reproduce the experimental binding energy and to reproduce adequately the bulk modulus as compared with those obtained using the other forms of $S_{ll'm}$.

It can be said that mainly E_{ov} and E_{cov} dominate the binding energy and the structural properties in all cases. E_{ov} and E_{cov} depend on volume as analysed in section 3. In SiC, E_{Mad} does not depend so much on volume and is only a small part of the binding energy. However, it should be noted that this is the result in the perfect crystal.

In figure 1, E_{pro} increases gradually with decreasing volume in Si, SiC and C. E_{pro} is the promotion energy in Si and C. In SiC, E_{pro} contains the promotion energy and the effect of charge transfer. However, the latter is small because the large increase in the intra-atomic Coulomb energy in C counterbalances the energy gain by electron transfer from the atomic levels of Si to those of C. As shown by Paxton *et al* [28], we have also found that the s–p mixing increases with decreasing volume in Si, SiC and C, and this is the origin of the dependence of E_{pro} on volume because the s–p splitting in calculation of E_{pro} is a constant as shown in equation (9*b*). The dependence of the s–p mixing on volume in Si resembles well that in [28].

E_{Mad} in SiC does not seem to depend much on volume. As volume increases, E_{Mad} becomes slightly more negative and is a minimum at larger volume than the equilibrium

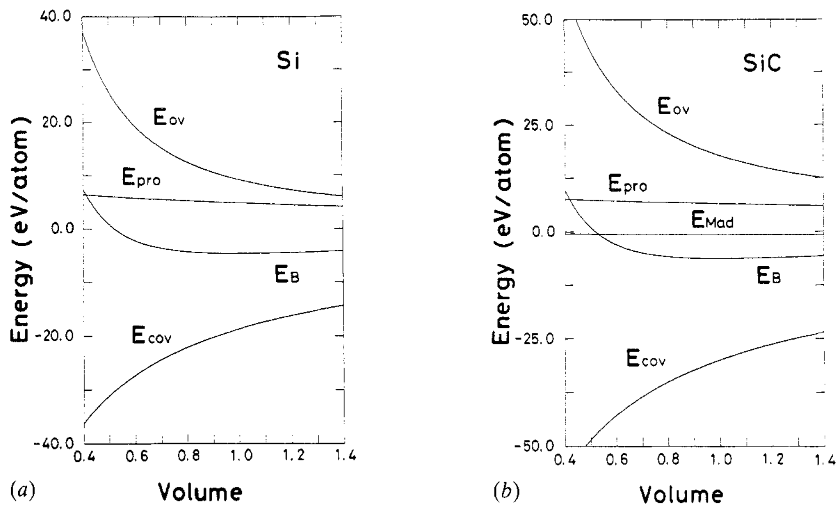

Figure 1. Energy–volume curves of the individual contributions to the binding energy of (*a*) Si and (*b*) SiC calculated by the SCTB method with the $p/r^4 + q$ form for overlap integrals.

volume. This is caused by the balance of the following two effects. The effective charge increases gradually with increasing volume. Inversely, the inter-atomic electrostatic function becomes weaker as volume increases.

The present dependence of the effective charge on volume is caused by the dependence of the off-diagonal Hamiltonian matrix element on the bond length, and is common in the tight-binding type theories. For example, the polarity in the bond orbital model [15], which is a measure of charge transfer, increases with increasing bond length because of decreasing magnitude of off-diagonal matrix element. This result is consistent with the experimental pressure dependence of the transverse effective charge e_T^* (the dynamic charge) in various compound semiconductors, where e_T^* decreases upon compression [30]. It can be said that ionicity decreases upon compression in most compounds. However, for SiC in the zincblende structure, an increase of e_T^* upon compression has been observed [31]. This experiment is inconsistent with the present calculated result and the prediction in usual tight-binding theories. Recently, Christensen *et al* [32] have obtained the polarity and ionicity in the tight-binding representation by transforming the results of the first-principles calculation using the linear muffin-tin orbital (LMTO) method, and have shown that the volume coefficients of the polarity and ionicity are negative in SiC differently from those of most compounds. This behaviour is explained by the special character of the first-row element C because of the absence of occupied core p orbitals.

Figures 2 and 3 show the binding energy–volume curves for several crystal structures of Si and SiC calculated using the $1/r^3$ form and the $p/r^4 + q$ form for $S_{ll'm}$. For the β-Sn structure, the axial ratio c/a is fixed to be 0.5516 in Si and 0.6 in SiC. For structures other than the zincblende and diamond structures, the second-neighbour interactions are included in the Hamiltonian and overlap matrices. However, the second-neighbour parameters $\eta_{ll'm}$ have been chosen according to [13], and so the contributions from the second neighbours are small in general.

For the results of Si in figure 2, the stability of the diamond structure and the possibility of a pressure-induced phase translation to the β-Sn structure are reproduced

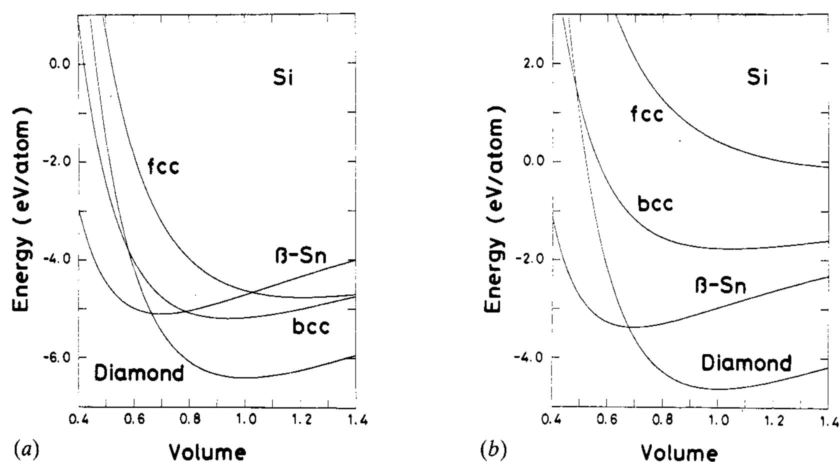

Figure 2. Binding energy of Si as a function of atomic volume for the diamond, β-Sn, BCC and FCC structures calculated by the SCTB method with (*a*) the $1/r^3$ form and (*b*) the $p/r^4 + q$ form for overlap integrals.

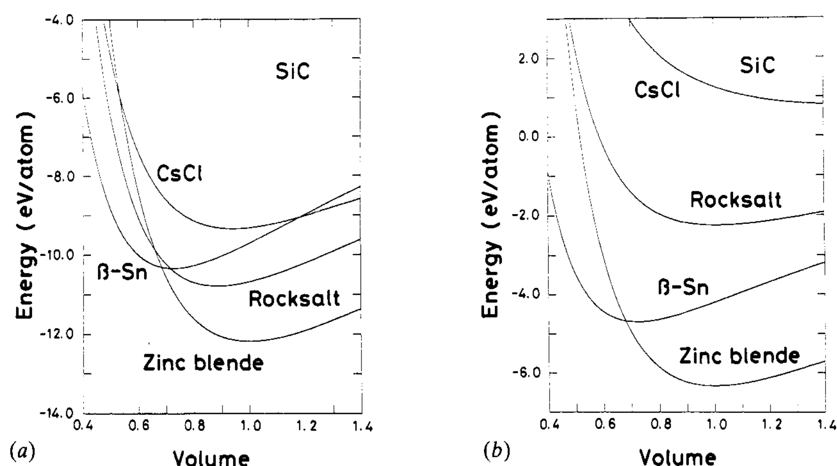

Figure 3. Binding energy of SiC as a function of atomic volume for the zincblende, β-Sn, rocksalt and CsCl structures calculated by the SCTB method with (*a*) the $1/r^3$ form and (*b*) the $p/r^4 + q$ form for overlap integrals.

in both cases of the forms of $S_{ll'm}$. It can be said that the results for the fourfold-coordinated structures (the diamond and the β-Sn structure) in figures 2(*a*) and (*b*) agree qualitatively with those calculated by the density-functional theory [33]. The results using the $1/r^3$ form are comparable with those obtained by Paxton and Sutton [29] using a $1/r^5$ repulsive potential. As well as the results in [29], the energies of the close-packed structures are poorly reproduced in figure 2. Especially, the energies of the close-packed structures calculated using the $p/r^4 + q$ form are much higher. This is because E_{ov} using the $p/r^4 + q$ form is overestimated for large r and is counted for a large number of neighbours in the close-packed structures.

Table 6. Breakdown of the energy differences between the diamond and wurtzite structures of Si and between the zincblende and wurtzite structures of SiC. All the values are calculated using the $1/r^3$ form for overlap integrals. All energies are in eV per two atoms.

Structure	E_B	s–p mixing	E_{pro}	E_{cov}	E_{ov}	E_{Mad}	Effective charge
Si							
Diamond	−12.8069	1.8717	9.5917	−37.3310	14.9324	—	—
Wurtzite	−12.8013	1.8741	9.6073	−37.3398	14.9312	—	—
SiC							
Zincblende	−24.3626	2.1935	12.8495	−59.7213	23.9793	−1.4702	0.4498*e*
Wurtzite	−24.3636	2.1965	12.8690	−59.7338	23.9770	−1.4758	0.4504*e*

The results of SiC in figure 3 are similar to those of Si. The energies of the close-packed structures calculated using the $p/r^4 + q$ form are much higher for the above-mentioned reason. The results in both forms of $S_{ll'm}$ show the stability of the zincblende structure and the possibility of a pressure-induced phase translation to the β-Sn structure. The result is consistent with the general relation of phase stability to ionicity [34]. However, the *ab initio* calculations [32, 35] have shown the possibility of a pressure-induced phase translation not to the β-Sn structure but to the rocksalt structure, where the ionic-like charge distribution keeps the semiconducting behaviour in the rocksalt structure and stabilises the rocksalt structure as compared with the β-Sn structure [35]. These behaviours are also explained by the fact that C is a first-row element and does not contain occupied core p orbitals. In the present results using the $1/r^3$ form, the minimum energy of the rocksalt structure is indeed lower than that of the β-Sn structure, but the electronic structure of SiC in the rocksalt structure is metallic and the phase translation to the rocksalt structure could not be reproduced.

We have calculated the energies of the wurtzite structures of Si and SiC with the same equilibrium volume as the diamond and zincblende structures using the $1/r^3$ form for $S_{ll'm}$. The axis ratio is fixed to be ideal. Table 6 shows the results.

For Si, the diamond structure is more stable than the wurtzite structure by 0.0055 eV per two atoms, although the energy difference is 0.02 eV per two atoms in the density-functional calculation [36]. The results can be analysed similarly to Paxton [37]. It can be said that the inter-atomic bonding is stronger in the wurtzite structure than in the diamond structure. This makes E_{cov} more negative in the wurtzite structure, but makes E_{pro} larger in the wurtzite structure because of the larger s–p mixing as shown in table 6. In addition, E_{ov} is larger in the diamond structure than in the wurtzite structure due to the s–p mixing because f_s in equation (7) is larger than f_p in the tetrahedral structure. The value of the binding energy difference between the diamond structure and the wurtzite structure is determined by the delicate balance of these three energy terms. It is probable that the value of the energy difference may be much influenced by the tight-binding parameters such as $E^0_{i\alpha}$, $\eta_{ll'm}$ and so on. In order to obtain more quantitative results, it should be important to use the parameters that can well reproduce the valence band structures of both the diamond and wurtzite structures.

For SiC, the present result shows that the wurtzite structure is more stable than the zincblende structure by 0.0009 eV per SiC pair. However, the wurtzite structure is higher in energy by 0.006 eV per SiC pair in the density-functional calculation [35], although

this value is at the limits of the accuracy of the calculations. The quantitative reliability of the present method is not so good, and it might be necessary to use another set of parameters in order to obtain more quantitative results as discussed above. However, it should be noted that the extremely small energy difference between the zincblende structure and the wurtzite structure in SiC is reproduced qualitatively in the present method. This can be analysed similarly to that of Si. As shown in table 6, the roles of the respective terms E_{pro}, E_{cov} and E_{ov} for the relative stability between the two structures are similar to those in Si. The total balance of these three terms in the two structures of SiC makes the zincblende structure more stable as well as in the case of Si. Thus it can be said that the effect of E_{Mad} is essential in stabilising the wurtzite structure and making the energy difference between the two structures of SiC extremely small. The effective charge is a little larger in the wurtzite structure in the present calculation. The wurtzite structure is more favourable for the inter-atomic electrostatic interaction, and is known to be stable for compounds with larger ionicity than that of compounds in the zincblende structure [38]. In this way, the small stacking fault energy in SiC and the extremely small energy difference between SiC polytypes seem to be explained from the viewpoint of the balance between E_{Mad} and the other terms in the present theoretical scheme.

5. Discussion

In order to apply the SCTB method to lattice defects in SiC, we have examined mainly the functional forms for the overlap integrals with use of ones by Majewski and Vogl for the other parameters and functional forms so as to reproduce the basic properties of Si, SiC and C. It can be said that the $1/r^2$ form of overlap integrals is suitable for calculations of structural properties of SiC and C and that the $1/r^3$ form is suitable for Si. And we have found that the $p/r^4 + q$ form is useful for representing structural properties of all Si, SiC and C, where the thermodynamic stability condition of SiC for Si and C is satisfied. This is important in treating lattice defects containing wrong bonds such as grain boundaries in SiC.

The nature of bonding and the phase stability in Si and SiC have been analysed by the SCTB method using the present functional forms and parameters. The energies and the nature of bonding of the fourfold-coordinated structures in Si and SiC are qualitatively reproduced by using the $1/r^3$ forms or the $p/r^4 + q$ form for overlap integrals. However, the energies and equilibrium volumes of close-packed structures are poorly reproduced. Thus it is necessary to be careful in use of the present functional forms for largely distorted systems in Si and SiC.

It should be noted that the $p/r^4 + q$ form for overlap integrals has been found phenomenologically on the assumption that there should exist simple universal forms such as $p/r^m + q/r^n$ so as to represent the binding energies and the bulk moduli of all Si, SiC and C. The $p/r^4 + q$ form itself does not necessarily have a physical significance nor give the best fit. However, it is certain that this form for overlap integrals coupled with other functional forms and parameters in the SCTB method can give relatively correct structural properties of Si, SiC and C at least where all the atoms are fourfold-coordinated, which is satisfied in a model of a grain boundary in our following paper.

Of course, in order to obtain more quantitative results within the present theoretical scheme, it should be necessary to choose functional forms and parameters for respective systems differently from the universal forms and parameters used in the present paper. Especially in order to represent the special characters of SiC caused by the first-row

element C, it might be inadequate to use the universal scaling laws of the two-centre integrals of the Hamiltonian and the overlap integrals as in the present paper.

With regard to structures other than the fourfold-coordinated ones, new transferable tight-binding models have recently been proposed for Si [39, 40]. In these models, the functional forms of the two-centre integrals of the Hamiltonian and the repulsive potentials are given by multiplying the usual functional forms by attenuation functions, and the behaviour of the two-centre integrals and the repulsive potentials for large distances is modified and these are smoothly truncated within proper distances. Thus the binding energies and the equilibrium volumes of close-packed structures can be well reproduced as well as the fourfold-coordinated structures. These types of functional forms of the two-centre integrals of the Hamiltonian and the overlap integrals must improve the representation of the close-packed structures in the present SCTB method, which will be necessary in applying the SCTB method for largely distorted systems or close-packed structures in future.

Finally, we should comment on the advantages of the present SCTB method over the TBB model [6]. The main difference between these two methods is the treatment of the effective atomic charges and the interactions between them. In the TBB model, the local charge neutrality is imposed as an approximate self-consistency and the on-site elements are adjusted so as to prevent charge transfer. The electron–electron interactions are included only in the site energy. In the SCTB method, the effective atomic charges are calculated self-consistently and the inter-atomic electrostatic interactions between them are calculated as E_{Mad} as well as the intra-atomic electrostatic interactions in E_{pro}. We agree that the local charge neutrality and the TBB model are effective in metals, metallic compounds and semiconductors such as Si. However, the validity of the local charge neutrality and the TBB model is doubtful in sp-bonded compounds with both ionic and covalent characters where charge transfer exists as compared with the superposition of the neutral atomic charges.

Of course, charge density in solids cannot be partitioned among atoms in an unambiguous way in general, and it might be possible to find a division of the charge density into the atomic regions so as to maintain the local charge neutrality in the respective regions. Thus we do not deny the possibility that the inter-atomic electrostatic interactions in the SCTB method could be incorporated in the TBB model as another term such as the site energy. In such cases, the difference between the TBB model and the SCTB method would be only the division of the binding energy into different terms. However, we insist that the SCTB method is more useful and superior in dealing with sp-bonded compounds with both ionic and covalent characters, because many properties of sp-bonded compounds can be effectively explained by incorporating the viewpoint of the interactions between the effective atomic charges and the physical origins of several properties cannot be explained from the viewpoint of the local charge neutrality. This is more important in treating lattice defects or distorted systems.

For example, it has been shown that the phase transition from the zincblende structure to the rocksalt structure in III–V and II–VI compounds can be well explained as the balance between the inter-atomic electrostatic energy and the covalent energy within the frozen potential approximation in the LMTO method [32, 41]. It has been deduced that the inter-atomic electrostatic interactions stabilise the eclipsed configuration in the wurtzite structure more than the staggered configuration in the zincblende structure and govern the stacking fault energies in III–V and II–VI compounds [42]. Recently, it has been pointed out that the effective atomic charges and the interactions between them are important in determining the atomic structure of the

surfaces of compound semiconductors. Tsai *et al* [43] have shown by first-principles calculations that the relaxation angle within the rigid-rotation model of the (110) zincblende surface decreases with increasing ionicity of compounds because of the Coulomb forces between the surface anions and the cations lying in and below the surface. We think that it is possible to explain and reproduce all the above properties and phenomena within the SCTB method if the functional forms and parameters are determined properly, because the inter-atomic electrostatic interactions are directly incorporated in the SCTB method. However, we do not think that all the above properties and phenomena can be effectively represented within the local charge neutrality.

This point is also important in SiC. With regard to SiC, it should be noted that the effective atomic charges are not small. This charge transfer has been obviously observed as compared with the superposition of the neutral atomic charges in the first-principles charge-density calculations [32, 35], where the charge flow easily occurs because of the absence of core p orbitals in C and the compound has largely ionic properties as compared with the ionicity defined spectroscopically [38]. Thus it is essential to use the SCTB method for SiC. As shown in the preceding section, the special properties of SiC as compared with Si and C such as the small stacking fault energy and the extremely small energy difference between polytypes do not seem to be explained without incorporating the inter-atomic electrostatic energy. If the local charge neutrality is imposed for SiC, the centres of gravity of the on-site elements at Si and at C would be adjusted to be the same as each other to prevent charge transfer, and the properties of SiC would be reproduced as only the intermediate ones between Si and C.

In conclusion, the SCTB method is capable of treating systems with both ionic and covalent characters, and is also applicable to calculations of lattice defects or disordered systems, because atomic forces can be given very easily via the Hellmann–Feynman theorem in this method as well as in the other tight-binding theories. We have presented clearly the formulation of electronic structure, total energy and atomic forces in periodic systems with use of the supercell technique for defect calculations. By choosing adequate functional forms and parameters for the two-centre integrals of the Hamiltonian and the overlap matrix, the effective inter-atomic electrostatic function and so on, the SCTB method should be a powerful scheme for calculations of complex systems containing a large number of atoms with both ionic and covalent characters, which cannot be treated effectively by using the other tight-binding theories.

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