

## ***Ab initio* bond self-interaction correction calculation of tetrahedrally bonded semiconductors and its application to superlattices by the most localized linear muffin-tin orbital method**

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The band-gap energies of tetrahedrally bonded semiconductors are approximately reproduced by a local-density-functional *ab initio* calculation including a bond self-interaction correction based on the viewpoint of bond orbitals. The calculations are performed by the *ab initio* tight-binding method (the most localized linear muffin-tin orbital method including a real-space combined correction). Results of Si, GaAs, AlAs, and superlattices  $(\text{GaAs})_n(\text{AlAs})_n$  for  $n=1,2$  are presented. The energies of the band gaps and conduction-band levels agree with the results of other empirical calculations and experiments. The conduction-band minima for superlattices locate at different  $k$  points for  $n=1$  and 2.

### I. INTRODUCTION

A number of first-principle electronic structure calculations have been reported for various classes of materials, atoms, molecules, clusters, surfaces, and bulk solids. In principle, electronic structures of small finite systems can be calculated exactly by the Hartree-Fock (HF) configuration-interaction (CI) method. But for infinite systems with many-body effects, in other words, with correlation effects, the calculation of the HF-CI method is impossible. Accordingly, modern band-structure calculations are mostly based on the Kohn-Sham density-functional (DF) theory.<sup>1</sup> In this theory, a many-body system with correlation is mapped into a virtual noninteracting system, where the interaction energy of the real physical system is well approximated by a self-consistent one-body potential. In practice, we use a local approximation of the DF theory (LDF). These LDF calculations of metals involving transition metals have provided successful results as to their ground-state properties, such as the cohesive properties and the ground-state magnetization. However, the band-gap energies of semiconductors and insulators and ionization potentials of atoms are always underestimated. In recent years, many studies have been devoted to this band-gap problem. Perdew *et al.*<sup>2,3</sup> and Sham *et al.*<sup>4</sup> had, respectively, found the discontinuity of the exchange-correlation potential with respect to an infinitesimal change of an electron number. These studies have shown that an underestimated band-gap energy is not due to the local approximation but inherent to the DF theory. What we should do next is to calculate the discontinuity in the framework of the DF theory.<sup>5</sup> But in practice this approach seems to lose the advantages of a LDF method. So we follow another approach of Perdew and Zunger.<sup>6</sup> They selected a physical picture rather than the exactness of the framework of the DF theory. They imposed a condition on the exchange-correlation potential ( $x_c$  potential) so that a physical one-particle state should not interact with itself, in other words, a self-interaction (SI) energy of the physical state should vanish. This self-

interaction correction (SIC) formalism is out of the DF theory, because resulting one-particle potentials depend on the orbitals. Even so the results for this SIC LDF calculation of atoms are much better than the original LDF results. In this point this atomic SIC LDF procedure is practically useful and efficient. However, they had initially pointed out that the atomic SIC LDF calculation cannot be applied to infinite systems, because the atomic SIC term vanishes for infinitely extended states. Heaton *et al.*<sup>7</sup> used a nearly atomic SIC with the LCAO basis and obtained excellent results for large energy gaps of insulators. This procedure seems to be incapable of describing the narrow gaps of semiconductors. In this paper we present a simple and efficient SIC for bulk solids based on the bond orbitals, which we call the bond SIC, and we show that the bond SIC improves the underestimation of the LDF band-gap energies.

The calculation is performed by the most localized linear muffin-tin orbital (LMTO) method based on the atomic sphere approximation (ASA) including so-called combined correction terms.<sup>8-11</sup> This method is an accurate *ab initio* tight-binding method. The basis set is minimal and most localized within the framework of a linear method, and there is no empirical parameter. The system can be described by the real-space tight-binding parameters up to the third nearest-neighbor pairs.

The basic formulation of the most localized LMTO method is briefly presented in Sec. II. In Sec. III we discuss the SIC of bulk solids, and present an approximated bond SIC scheme used in the present work. In Sec. IV we apply this method to Si, GaAs, AlAs, and  $(\text{GaAs})_n(\text{AlAs})_n$ , for  $n=1,2$  and discuss them. We summarize the results in Sec. V.

### II. THE MOST LOCALIZED LMTO METHOD AND THE COMBINED CORRECTION

In this section we summarize the most localized linear muffin-tin orbital method (most localized LMTO) including the combined correction terms. There are many approaches for calculating electronic structures. By the

traditional APW or KKR methods we have to solve an energy-dependent secular equation to determine the energy eigenvalues, and the energy dependence has its rise in energy-dependent wave functions in an implicit way. In the linear method we expand wave functions in terms of energy deviation about the neighborhood of our interest. As a result, we get a homogeneous secular equation.<sup>8</sup> In the LMTO method, the space is divided into overlapping spheres (atomic spheres) having centers at atomic positions, then the secular equation is perfectly decomposed into two parts, i.e., a structure part (the structure constant) independent of the atomic character and potential-dependent parameters (the potential parameters) that have transparent physical meaning.

In the original LMTO method, it is formulated in a  $k$ -space representation. On the other hand, many empirical tight-binding calculations have been successfully reported for various materials. And it seems natural that the electronic structure is not affected by the farther environment even in a periodic system. This fact implies that the basic electronic structures of materials are approximately described by short-range interactions in a real space. This is realized in the most localized LMTO method.<sup>9–11</sup>

In this method the structure of the system is represented by the matrix  $\bar{S}$  having indices in a real space (the screened structure constant). This decays so rapidly in a real space that  $\bar{S}_{RR'}$  is almost zero for the fourth-nearest-neighbor pairs. The  $\bar{S}$  matrix satisfies the following Dyson type equation as

$$\bar{S} = S + \frac{1}{2}(S \bar{Q} \bar{S} + \bar{S} \bar{Q} S), \quad (2.1)$$

where matrix  $S$  is the bare structure constant which has an analytic expression and has a long-range tail. The diagonal matrix  $\bar{Q}$  is introduced to make  $\bar{S}$  localize and its elements are usually chosen as<sup>9</sup>

$$\bar{Q}_s = 0.3485, \quad \bar{Q}_p = 0.05303, \quad \bar{Q}_d = 0.010714. \quad (2.2)$$

The resulting Hamiltonian and overlap matrix are represented in the following tight-binding (two center) form:

$$H_{R'L';RL}^{(2)} = E_{vRL} \delta_{RR'} \delta_{LL'} + h_{R'L';RL}, \quad (2.3)$$

$$O_{R'L';RL}^{(2)} = \delta_{RR'} \delta_{LL'}, \quad (2.4)$$

where  $R$  denotes an atomic site and the  $L = (l, m)$  is an abbreviated notation of an azimuthal quantum number  $l$  and a magnetic quantum number  $m$ . The  $E_{vRL}$  is an energy where we linearize the  $L$  character wave function of  $R$  site. The reduced Hamiltonian  $h$  can be calculated in terms of the  $\bar{S}$  and some potential parameters. The above Hamiltonian is accurate in the second order of  $(E - E_{vRL})$  and the next-order terms can be included by the first-order perturbation theory.

The above formalism is called an atomic sphere approximation, because the space is decomposed into overlapping spheres (atomic spheres) and wave functions are neglected outside the atomic spheres. It is known that this ASA gives accurate results for a calculation of met-

als but poor for semiconductors especially for their band-gap energies.<sup>12</sup> So when we discuss the band-gap energy from the first principle, we have to include the correction to ASA (the combined correction and another third-order correction). In the most localized LMTO, this combined correction can be easily included in a real space by using the screened structure constant  $\bar{S}$ .

### III. DENSITY-FUNCTIONAL THEORY AND SIC OF BULK SOLIDS

In this section we summarize the Kohn-Sham density-functional theory and the band-gap problem, next we argue the self-interaction correction and explain our bond self-interaction correction approximation.

#### A. Atomic SIC and bond SIC

The ground-state property of a many-particle system is a unique functional of its density and the basic physical quantity is a particle density  $n(\mathbf{r})$ .<sup>1</sup> In the density-functional theory, we map a real physical system including many-particle effects into a virtual noninteracting system by a variational principle with the condition that their particle densities should be equal. This mapping is uniquely determined under some assumptions when the exchange-correlation energy functional  $E_{xc}[n]$  is given. But this xc energy functional is unknown for real physical systems and so we have to use a local approximation, which is called the local density-functional approximation or the local spin-density functional approximation (LSD). This procedure is simply an approximation in the practical density-functional calculation. As a result we construct the noninteracting system by a self-consistent calculation of the following one-particle equation:<sup>1</sup>

$$[-\frac{1}{2}\Delta + v_{\text{eff}}^{\sigma}(\mathbf{r})]\psi_{j\sigma}(\mathbf{r}) = \epsilon_j \psi_{j\sigma}(\mathbf{r}), \quad (3.1)$$

$$v_{\text{eff}}^{\sigma}(\mathbf{r}) = v(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{xc}}{\delta n_{\sigma}(\mathbf{r})}, \quad (3.2)$$

$$n(\mathbf{r}) = n_{+}(\mathbf{r}) + n_{-}(\mathbf{r}), \quad (3.3)$$

$$n_{\sigma}(\mathbf{r}) = \sum_{j:\text{occ}} |\psi_{j\sigma}(\mathbf{r})|^2, \quad (3.4)$$

where  $\sigma$  is the spin index and  $n_{\sigma}(\mathbf{r})$  is the electron density of  $\sigma$  spin.

This LSD theory is practically very useful in comparison with the HF-CI calculation and many first-principle calculations of electronic structures are successfully performed in various systems. Their results agree very well with experimental results. In principle, however, the LSD band energies have no rigorous meaning of the one-particle energies, and they have only a relation to their occupation numbers by the Janak's theorem.<sup>13</sup> The validity of the theory for their one-particle energies and the Fermi energy should be examined by a comparison with experimental results, and usually it is excellent for metals. But the calculated band-gap energies for semiconductors are always underestimated by 30–40%. Especially in the relativistic calculation, the band-gap

energies are more small and sometimes vanish. This is the "band-gap problem in the DF theory."

In the framework of the DF theory we can calculate a band-gap energy  $E_g$  of a semiconductor by the following expression:

$$E_g = I(M) - A(M), \quad (3.5)$$

$$= \varepsilon_{M+1}(M+\eta) - \varepsilon_M(M-\eta) \quad (\eta = +0), \quad (3.6)$$

$$\approx \varepsilon_{M+1}(M) - \varepsilon_M(M), \quad (3.7)$$

where  $M$  is a number of total electrons,  $I(M)$  and  $A(M)$ , are an ionization potential and an electron affinity of a  $M$ -electron system, and  $\varepsilon_N(M)$  is the  $N$ th lowest orbital energy of the  $M$ -electron system. The resulting band-gap energies of this calculation have an error systematically, and its origin is the replacement of Eq. (3.6) by Eq. (3.7). Then it is recognized that there is a finite discontinuity in an effective potential between the systems with infinitesimally different electron numbers.<sup>2-5</sup> The accurate expression is

$$E_g = \varepsilon_{M+1}(M) - \varepsilon_M(M) + C, \quad (3.8)$$

$$C = v_{\text{eff}}(M+\eta) - v_{\text{eff}}(M-\eta). \quad (3.9)$$

We notice that the finite constant change of the one-particle potential does not change the resulting one-particle wave function.

To obtain an accurate band-gap energy by the first-principle calculation, we have to calculate the discontinuity  $C$ , but it seems difficult to know the  $C$  in the LSD framework. Practically, it is worthwhile to give a method calculating the approximate band-gap energy efficiently and easily in the LSD scheme. So we propose a bond self-interaction correction and apply it to III-V and IV class semiconductors.

The original atomic SIC was introduced by Perdew *et al.*<sup>6</sup> In the LSD theory there is nonzero self-interaction energy even if there is only one particle in the system. The self-interaction energy for the one-particle state  $\psi_{j\sigma}(\mathbf{r})$  is defined as

$$\delta_{j\sigma} = E_{\text{xc}}^{\text{LSD}}[n_{j\sigma}, 0] + U[n_{j\sigma}], \quad (3.10)$$

$$n_{j\sigma}(\mathbf{r}) = |\psi_{j\sigma}(\mathbf{r})|^2, \quad (3.11)$$

$$U[n_{j\sigma}] = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{n_{j\sigma}(\mathbf{r}') n_{j\sigma}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}, \quad (3.12)$$

and when we interpret  $\psi_{j\sigma}$  as a physical state,  $\delta_{j\sigma}$  should be zero. This is the case of the HF theory. The SIC xc energy functional of Perdew *et al.* is defined as

$$E_{\text{xc}}^{\text{LSD-SIC}} = E_{\text{xc}}^{\text{LSD}} - \sum_{j,\sigma:\text{occ.}} \delta_{j\sigma}, \quad (3.13)$$

and the effective potential for  $j\sigma$  state is

$$v_{\text{eff } j\sigma}^{\text{SIC-LSD}}(\mathbf{r}) = v_{\text{eff}}^{\text{LSD}}(\mathbf{r}) + \Delta v_{\text{eff } j\sigma}^{\text{SIC}}, \quad (3.14)$$

$$\Delta v_{\text{eff } j\sigma}^{\text{SIC}} = - \left[ v_{\text{xc}}[n_{j\sigma}, 0] + \int d\mathbf{r}' \frac{n_{j\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right]. \quad (3.15)$$

By this definition of the SIC xc energy functional,  $\delta_{j\sigma}^{\text{SIC-LSD}} = 0$ . Their calculated results for atoms show

that the ionization energy and one-particle energies are well reproduced. But this atomic self-interaction potential depends on the orbital and the orthogonality of the orbitals is lost. Furthermore, their procedure cannot be applied to bulk systems in a simple form, because in the solids the one-particle state is the Bloch state, and the self-interaction  $\delta_{j\sigma}$  for the Bloch state extending over a whole space vanishes in a way of

$$\Delta v_{\text{eff } j\sigma}^{\text{SIC}} = O(V^{-1/3}) \rightarrow 0$$

(where  $V$  is a volume of the system).

Several SIC calculations for bulk solids are reported by Heaton *et al.*<sup>7</sup> and Hamada *et al.*<sup>14</sup> Heaton's SIC is formulated in Wannier orbitals, they used atomic orbitals in the LCAO scheme and got good results for the large gaps of insulators. Their improvement is a natural extension of the atomic SIC. Hamada *et al.* calculated the band gaps of semiconductors in the SIC-LAPW method, where an atomic SIC is included only in the LAPW muffin-tin sphere, and the SIC effect seems to depend on the choice of radii of muffin-tin spheres. We wish to propose a more appropriate SIC procedure which can be applicable to semiconductors.

Here we suppose a limiting case where isolated atoms are periodically arranged with a macroscopic lattice constant. Then the resulting LSD electronic band structures show zero-width bands at atomic energy levels. The ionization energy or the band-gap energy of the systems are underestimated as in atomic calculations. Furthermore, the atomic SIC is zero for the Bloch state, that is an eigenstate. However, the atoms are isolated and Perdew's atomic SIC should effectively improve the one-particle energies. In this case, all states at different  $k$  points degenerate and the localized Wannier functions are atomic orbitals and also eigenstates. Then, naturally, we can use the SIC in this representation, and get good results identical to atomic cases.

Next we introduce an infinitesimally small overlap between the atomic orbitals, then the resulting band structure has a corresponding small dispersion, but the Wannier function is not an eigenstate. The unique one-particle eigenstate is a Bloch state, and the resulting original SIC is zero, so the SIC calculation does not work. But this is unphysical. For an atomic system, one of the reasons why the atomic SIC brings good results is the atomic SIC potential gives physically natural xc hole and the potential has an asymptotic behavior of  $\rightarrow 1/r$  in comparison with an asymptotical behavior of the original LDF potential  $\rightarrow 0$ . We know that, in the SIC-LSD calculation, we have to use physically natural states for the one-particle density. In other words, for the calculations of SIC, we should use Bloch states for metals, localized Wannier states for insulators, and atomic orbitals for atoms.

For III-V and IV class semiconductors, Harrison's bond orbital model<sup>15</sup> provides a physical picture and calculations show localized bond charge densities. These facts show the bond orbital picture by Harrison is a physical one in this class, and we use the bond orbital densities to calculate the SIC.

For core electrons, we should use the atomic SIC.

For conduction bands we do not correct the one-particle LSD energies, because there is no occupancy in the conduction bands and the SIC should be zero. This procedure describes more or less the discontinuity of the potential. Then the Hamiltonian of this system is written as

$$H = H^{\text{LSD}} + \Delta V_{\text{atomic}}^{\text{SIC}} + \Delta V_{\text{bond}}^{\text{SIC}}, \quad (3.16)$$

where  $H^{\text{LSD}}$ ,  $\Delta V_{\text{atomic}}^{\text{SIC}}$ , and  $\Delta V_{\text{bond}}^{\text{SIC}}$  are, respectively, the original LSD Hamiltonian, the atomic SIC potential for core electrons, and the bond SIC potential for valence bands.

### B. Approximated bond SIC in tetrahedrally bonded semiconductors

Here we explain the approximation used in the bond SIC procedure in the most localized LMTO scheme. We introduce a bond SIC for valence bands by the first-order perturbation theory. The basic idea is as follows.

First we calculate a bond charge distribution and secondly we include the bond SIC potential in the LSD Hamiltonian by the first-order perturbation theory.

The eigenvalue of the  $j$  valence band at the  $k$  point  $E_v^{\text{BSIC}}(kj)$  in the bond SIC calculation is given as

$$E_v^{\text{BSIC}}(kj) = E_v^{\text{LSD}}(kj) + \Delta E(kj), \quad (3.17)$$

where  $E_v^{\text{LSD}}(kj)$  is an eigenvalue of LSD calculation, and  $\Delta E(kj)$  is the effect of a bond SIC potential defined by the first-order perturbation theory as

$$\Delta E(kj) = \langle \psi_j^k | \Delta V_{\text{bond}}^{\text{SIC}} | \Psi_j^k \rangle. \quad (3.18)$$

In the most localized LMTO, Bloch function  $\psi_j^k$  is given as

$$\psi_j^k = \frac{1}{\sqrt{N}} \sum_{\mathbf{T}} e^{i\mathbf{k}\cdot\mathbf{T}} \sum_{t,L} |\bar{\chi}\rangle_{tL} \bar{u}_{tL;kj}, \quad (3.19)$$

where  $N$  is the number of the unit cells,  $\mathbf{T}$  is a lattice translation vector,  $|\bar{\chi}\rangle_{tL}$  is a localized LMTO base of the  $t$  atom and  $\bar{u}_{tL;kj}$  is a coefficient of the wave function normalized to unity as

$$\sum_{tL} |\bar{u}_{tL;kj}|^2 = 1. \quad (3.20)$$

The bond SIC potential  $\Delta V_{\text{bond}}^{\text{SIC}}$  is given as a sum of contributions of each bond as

$$\Delta V_{\text{bond}}^{\text{SIC}} = \sum_{b_{tt'}} |b_{tt'}\rangle \Delta V^{b_{tt'}} \langle b_{tt'}|. \quad (3.21)$$

Each bond is denoted by  $b_{tt'}$  and  $t, t'$  specify the two atoms forming the bond. A bond orbital  $|b_{tt'}\rangle$  is defined as

$$|b_{tt'}\rangle = s_t |h_t\rangle + s_{t'} |h_{t'}\rangle, \quad (3.22)$$

$$s_t^2 + s_{t'}^2 = 1, \quad (3.23)$$

$$\frac{s_t^2}{s_{t'}^2} = \frac{\sum_{k,L} |\bar{u}_{tLkj}|^2}{\sum_{k,L} |\bar{u}_{t'Lkj}|^2}, \quad (3.24)$$

where  $|h_t\rangle$  is one of  $sp^3$  hybridized orbitals of the  $t$  kind atom approximately expressed as

$$|h_t\rangle = \frac{1}{\sqrt{4}} [ |\bar{\chi}\rangle_{s;t} \pm |\bar{\chi}\rangle_{px;t} \pm |\bar{\chi}\rangle_{py;t} \pm |\bar{\chi}\rangle_{pz;t} ]. \quad (3.25)$$

The bond orbital SIC potential has been given as the sum of the contribution from each atomic sphere as

$$\Delta V^{b_{tt'}} = s_t^2 \langle h_t | \Delta \tilde{V}^{b_{tt'}(t)} | h_t \rangle + s_{t'}^2 \langle h_{t'} | \Delta \tilde{V}^{b_{tt'}(t')} | h_{t'} \rangle, \quad (3.26)$$

and  $\Delta \tilde{V}^{b_{tt'}(t)}$  is the bond SIC potential within the  $t$  kind atomic sphere as

$$\Delta \tilde{V}^{b_{tt'}(i)}(\mathbf{r}) = - \left[ \int_{iMT} d\mathbf{r}' \frac{n^{b_{tt'}(\mathbf{r}')} }{|\mathbf{r}-\mathbf{r}'|} + v_{xc}[n^{b_{tt'}}, 0] + \int_{i'MT} d\mathbf{r}' \frac{n^{b_{tt'}(\mathbf{r}')} }{|\mathbf{r}-\mathbf{r}'|} \right] \quad (i=t \text{ or } t'), \quad (3.27)$$

The  $n^{b_{tt'}(\mathbf{r}')}$  is a bond charge density, which is the sum of the valence-band atomic sphere charge at  $t$  and  $t'$  atoms and normalized to unity in the  $b_{tt'}$  bond. The integration in Eq. (3.26) is performed within each  $i$  atomic sphere. The last term of Eq. (3.27) is an electrostatic potential by the bond charge in the  $i'$  atomic sphere, where the  $i'$  atom is a counterpart of the  $i$  atom of the bond.

Then we find that  $\Delta E(kj)$  is given as

$$\Delta E(kj) = \sum_{L,t,b_{tt'}} |\langle \bar{\chi}_{tL} | b_{tt'} \rangle|^2 \Delta V^{b_{tt'}} |\bar{u}_{tLkj}|^2, \quad (3.28)$$

$$= \sum_L \sum_t |\bar{u}_{tLkj}|^2 \frac{1}{4} s_t^2 \sum_{b_{tt'}} \Delta V^{b_{tt'}}, \quad (3.29)$$

where we use the fact that  $|\bar{\chi}\rangle_{tL}$  is small enough to be neglected outside the  $t$  atomic sphere.

## IV. RESULTS AND DISCUSSION

In this section first we show the results of the bond SIC calculation for tetrahedrally bonded semiconductors of class IV and III-V, Si, GaAs, and AlAs, and apply the bond SIC to superlattices  $(\text{GaAs})_n(\text{AlAs})_n$  for  $n=1,2$ . In this calculation we use the most localized LMTO method with the combined correction terms. The SIC calculation is not so much affected by a choice of the local xc potential, then we use a Barth-Hedin local xc potential. We include a scalar-relativistic effect but the spin-orbit coupling is neglected.

The structures of these materials are diamond or zinc-blende structures and these structures are so sparse that the combined correction does not work well. Then

TABLE I. Lattice constants and radii of atomic spheres.

Material	Atom	Atomic sphere radii (a.u.)	Lattice constant (a.u.)
Si	Si	2.526	5.1300
	empty atom	2.526	
GaAs, AlAs, (GaAs) <sub>n</sub> (AlAs) <sub>n</sub>	Ga,Al	3.000	5.3415
	As	3.000	
	empty atom	2.109	

we have to introduce some empty atoms as usual<sup>12,16</sup> to pack the whole space densely, and the resulting structure becomes a body centered cubic lattice. The input data for the calculation are values of lattice constants, atomic numbers, and atomic sphere radii (Table I).

First we iteratively calculate  $\bar{S}$  by Eq. (2.1) and the analytic  $S$ , then we calculate the real-space combined corrections by using  $\bar{S}$  and  $\bar{Q}$ . We can calculate these matrices efficiently in a real space. Then the lattice Fourier transformation of the tight-binding Hamiltonian brings a band structure. In the calculation, we use a frozen-core approximation within the core electron configuration summarized in Table II. We use three energy panels except a case of two energy panels for Si, and in each panel we linearize an energy dependence of the wave function around fixed  $E_{v,RL}$ .

#### A. Si

Si has an indirect energy gap and a conduction-band minimum locates at  $\mathbf{k} = (2\pi/a)(0.88, 0.0, 0.0)$ . The bond SIC lowers the valence band and the resulting band gap energy is 1.27 eV. In a monatomic system, our bond SIC shift of the valence band is uniform. The energy levels of the high symmetric points are listed in Table III, where the results of the LMTO-LDF method by Glötzel *et al.*<sup>17</sup> and the results of empirical nonlocal pseudo-potential method by Chelikowsky *et al.*<sup>18</sup> are also listed for a comparison. In Tables III–V energy levels are measured from the maxima of valence bands. This shows that the accuracy of the calculation of the LDF is much improved in the bond SIC calculation.

#### B. GaAs and AlAs

The band structure is shown in Fig. 1, where the hatched area shows the bond SIC effect. In this case we have to relax the shallow Ga  $d$  level. Without this core relaxation, the band gap would be much wider.<sup>16</sup> The minimum of the conduction band is at the  $\Gamma$  point and the band-gap energy of a simple LDF is very small, 0.097 eV. The bond SIC shift of the valence band is not uniform due to the difference of the electron affinity.

TABLE II. Core electron configurations used in the calculations.

Si:	$(1s)^2(2s)^2(2p)^6$
Ga:	$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6$
Al:	$(1s)^2(2s)^2(2p)^6$
As:	$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^{10}$

TABLE III. Energy eigenvalues of Si.

Level	Si energy eigenvalues (eV)		
	Empirical nonlocal pseudopotential (Ref. 18)	LMTO (Ref. 17)	Scalar relativistic LDF + bond SIC (present work)
$\Gamma_1^v$	-12.36	-11.87	-11.92
$\Gamma_{25'}^v$	0.00	0.00	0.00
$\Gamma_{15}^c$	3.43	2.59	3.51
$\Gamma_2^c$	4.10	3.11	3.95
$X_1^v$	-7.69	-7.75	-7.92
$X_4^v$	-2.86	-2.72	-2.82
$X_1^c$	1.17	0.62	1.37
$L_2^v$	-9.55	-9.53	-9.74
$L_1^v$	-6.96	-6.93	-7.01
$L_3^v$	-1.23	-1.05	-1.11
$L_1^c$	2.23	1.57	2.16
$L_3^c$	4.34	3.51	4.04

The resulting bond SIC band gap is 1.05 eV (an experimental value is  $\sim 1.5$  eV). The energy levels at high symmetry points are listed in Table IV, where an empirical pseudo-potential calculation of Chelikowsky *et al.*<sup>18</sup> and a full-relativistic LMTO-LSD calculation of Christensen<sup>16</sup> are also listed for a comparison. Comparing these results, relative valence-band levels agree well with each other. But for the band-gap energies, results of the bond SIC show improvement of the underestimation of the LDF results and agree well with the empirical results.

For AlAs, we list the similar results in Table V. In this case the bond SIC energy levels also agree with the results of the empirical calculations.<sup>19–21</sup>

TABLE IV. Energy eigenvalues of GaAs. In Refs. 16 and 18, the calculations are done by the full-relativistic formulation including the spin-orbit interaction. In this table the split levels by the spin-orbit interaction are averaged with the weighting factors of degeneracy.

Level	GaAs energy eigenvalues (eV)		
	Empirical nonlocal pseudopotential (Ref. 18)	Full relativistic LSD (Ref. 16)	Scalar relativistic LDF + bond SIC (present work)
$\Gamma_1^v$	-12.38	-12.67	-12.94
$\Gamma_{15}^v$	0.00	0.00	0.00
$\Gamma_1^c$	1.69	0.43	1.05
$\Gamma_{15}^c$	4.83	3.92	4.45
$X_1^v$	-9.66	-10.31	-10.80
$X_3^v$	-6.71	-6.88	-6.95
$X_5^v$	-3.12	-2.69	-2.84
$X_1^c$	2.21	1.23	1.94
$X_3^c$	2.56	1.46	2.11
$L_1^v$	-10.78	-11.02	-11.47
$L_2^v$	-7.01	-6.76	-6.86
$L_3^v$	-1.15	-1.11	-1.20
$L_1^c$	2.00	0.85	1.48

TABLE V. Energy eigenvalues of AIAs.

Level	AIAs energy eigenvalues (eV)			
	LDF bond SIC (present work)	Empirical pseudopotential (Ref. 19)	Empirical pseudopotential (Ref. 20)	OPW (Ref. 21)
$\Gamma_1^v$	-12.28	-11.57	-11.56	-11.48
$\Gamma_{15}^v$	0.00	0.00	0.00	0.00
$\Gamma_1^c$	2.74	2.81	3.21	2.50
$\Gamma_{15}^c$	5.06	4.21	4.57	4.57
$X_1^v$	-10.69	-8.96	-9.42	-9.61
$X_3^v$	-5.61	-6.45	-5.55	-5.20
$X_5^v$	-2.38	-2.32	-1.97	-2.01
$X_1^c$	1.83	2.21	2.25	2.38
$X_3^c$	2.74	2.89	2.62	2.86
$L_1^v$	-11.16	-9.85	-10.07	-10.14
$L_2^v$	-5.85	-6.04	-5.52	-5.22
$L_3^v$	-0.88	-0.98	-0.70	-0.80
$L_1^c$	2.76	2.48	2.76	2.57

### C. Superlattice $(\text{GaAs})_n(\text{AIAs})_n$

From the above calculations, our bond SIC improves the underestimation of the conduction-band levels of LSD calculations. We think that this approximation is appropriate and practically efficient. Next we apply this method to more complicated superlattice cases. In the most localized LMTO, its structure-dependent part is calculated in a real space and this scheme does not depend on the atomic character (except for atomic sphere radii). This property enables us to calculate an electron-

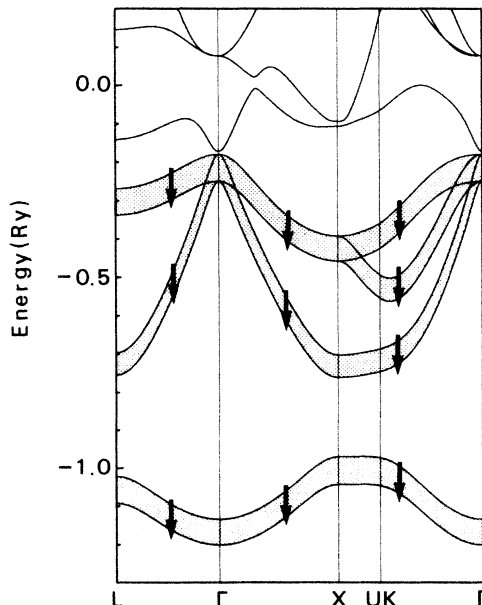


FIG. 1. Band structure of GaAs along symmetric lines. Bond SIC effect is shown by arrows.

ic structure of superlattices very easily. We can construct a structure constant and combined correction matrices of the superlattices from the structure constant of its simple substructure.

The minimum of the conduction band locates at the  $L$  point of a fcc Brillouin zone for  $n=1$  and the  $\Gamma$  point for  $n=2$ . The energy levels of fcc high-symmetric points are listed in Table VI together with results of the empirical  $X\alpha$  method. Our results show the conduction band minimum shifts from the  $L$  point to the  $\Gamma$  point by the  $\Gamma$ - $X$  interaction, and our band-gap energies show the same tendency as the empirical  $X\alpha$  calculation.<sup>22</sup>

The band-gap energies by the LDF and the bond-SIC-LDF calculation in the present work are listed in Table VII and this shows the usefulness of the bond SIC.

### V. CONCLUSIONS

In this paper we proposed the bond SIC and applied this to several semiconductors. We proposed an approximated procedure to calculate the band-gap energies of tetrahedrally bonded semiconductors. In the SIC calculation, we should use physically natural states for the

TABLE VI. Gap energies of superlattices  $(\text{GaAs})_n(\text{AIAs})_n$  at high symmetric points (fcc).

Gap energies (eV) at high symmetric points				
	Method	$\Gamma$ point	$L$ point	$X$ point
$n=1$	bond-SIC-LDF <sup>a</sup>	1.60(0.65)	1.51(0.56)	1.89(0.94)
	$X\alpha^b$	1.76	1.68	1.76
$n=2$	bond-SIC-LDF <sup>a</sup>	1.73(0.74)	2.01(1.02)	1.90(0.91)
	$X\alpha^b$	1.97	2.10	2.13

<sup>a</sup>The values within the parentheses are those without SIC.

<sup>b</sup>Reference 22.

TABLE VII. Self-interaction correction and band-gap energy.

	Band-gap energies (eV) of semiconductors		Expt.
	LDF	Bond SIC	
GaAs	0.097	1.05	1.52
AlAs	0.86	1.83	2.25
Si	0.43	1.27	1.17
(GaAs) <sub>1</sub> (AlAs) <sub>1</sub>	0.56	1.51	
(GaAs) <sub>2</sub> (AlAs) <sub>2</sub>	0.74	1.73	

one-particle density, i.e., the Bloch states for metals, the Wannier states for insulators, and the atomic orbitals for atoms. For the tetrahedrally bonded semiconductors this state is the bond orbital. We introduced the SIC po-

tential in this bond charge distribution and then calculate the effect of the SIC potential to the Bloch states by the first-order perturbation theory.

The bond SIC is formulated in the most localized LMTO scheme. The most localized LMTO method is accurate enough to discuss the band-gap energies when the combined correction terms are included. This real-space method is especially efficient in the calculation of superlattices. The calculations for the class IV and III-V semiconductors, Si, GaAs, and AlAs, show that the bond SIC improves the underestimation of the LSD band gap. Next we apply this method to the superlattice (GaAs)<sub>n</sub>(AlAs)<sub>n</sub> and get the appropriate results for their band-gap energies and the position of a conduction-band minimum.

- <sup>1</sup>W. Kohn and P. Vashishta, in *Theory of the Inhomogeneous Electron Gas*, edited by S. Lundqvist and N. H. March (Plenum, New York, 1983), p. 79.
- <sup>2</sup>J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, *Phys. Rev. Lett.* **49**, 1691 (1982).
- <sup>3</sup>J. P. Perdew and M. Levy, *Phys. Rev. Lett.* **51**, 1884 (1983).
- <sup>4</sup>L. J. Sham and M. Schluter, *Phys. Rev. Lett.* **51**, 1888 (1983).
- <sup>5</sup>W. Kohn, *Phys. Rev. B* **33**, 4331 (1986).
- <sup>6</sup>J. P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).
- <sup>7</sup>R. A. Heaton, J. G. Harrison, and C. C. Lin, *Phys. Rev. B* **28**, 5992 (1983).
- <sup>8</sup>O. K. Andersen, *Phys. Rev. B* **12**, 3060 (1975).
- <sup>9</sup>O. K. Andersen, O. Jepsen, and D. Glötzel, in *Highlight of Condensed-Matter Theory*, edited by F. Bassani, F. Fumi, and M. Tosi (North-Holland, Amsterdam, 1985), p. 59.
- <sup>10</sup>T. Fujiwara, *J. Non-Cryst. Solids* **61&62**, 1039 (1984).
- <sup>11</sup>O. K. Andersen and O. Jepsen, *Phys. Rev. Lett.* **53**, 2571

- (1984).
- <sup>12</sup>T. Jarlborg and A. J. Freeman, *Phys. Lett.* **26**, 349 (1979).
- <sup>13</sup>J. F. Janak, *Phys. Rev. B* **18**, 7165 (1978).
- <sup>14</sup>N. Hamada and S. Ohnishi, *Phys. Rev. B* **34**, 9042 (1986).
- <sup>15</sup>W. A. Harrison and S. Ciraci, *Phys. Rev. B* **10**, 1516 (1973).
- <sup>16</sup>N. E. Christensen, *Phys. Rev. B* **30**, 5753 (1984).
- <sup>17</sup>D. Glötzel, B. Segal, and O. K. Andersen, *Solid State Comm.* **36**, 403 (1980).
- <sup>18</sup>J. R. Chelikowsky and M. L. Cohen, *Phys. Rev. B* **14**, 556 (1976).
- <sup>19</sup>E. Caruthers and P. J. Lin-Chung, *Phys. Rev. B* **17**, 2705 (1978).
- <sup>20</sup>E. Hess, I. Topol, K.-R. Schulze, H. Neumann, and K. Uger, *Phys. Status Solidi B* **55**, 187 (1973).
- <sup>21</sup>D. J. Stukel and R. N. Euwema, *Phys. Rev.* **188**, 1173 (1969).
- <sup>22</sup>T. Nakayama and H. Kamimura, *J. Phys. Soc. Jpn.* **54**, 4726 (1985).

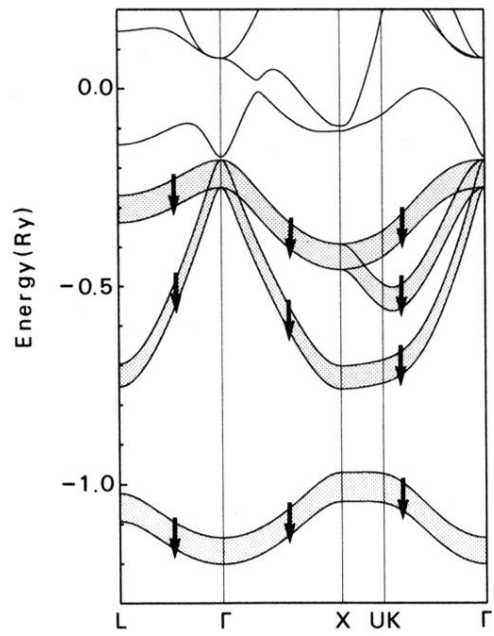


FIG. 1. Band structure of GaAs along symmetric lines. Bond SIC effect is shown by arrows.