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# Average bonding–antibonding energy at semiconductor heterojunctions and its application to calculating the valence band offset

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**Abstract.** In this paper, the alignment of the average bonding–antibonding energy  $E_m$  between the two sides of heterojunctions and other relevant behaviour have been investigated. This study is based on the peculiarity of the atomic sphere approximation in the linear muffin-tin orbital band-structure calculation. Using  $E_m$  as an energy reference, we have determined the valence band offset  $\Delta E_v$ -values for 16 heterojunctions. The calculated results are in excellent agreement with the available experimental data, and the computational effort required is very small.

## 1. Introduction

In several theoretical models of heterojunction valence band offsets  $\Delta E_v$ , a reference level which is aligned on the two sides of the heterojunctions was researched in order to determine the  $\Delta E_v$ -value. For example, the effective midgap energy  $E_B$  of the charge-neutrality-point (CNP) model [1, 2] and  $E_D$  of the dielectric-midgap-energy model (DME) [3] as well as the average  $sp^3$  hybrid energy  $E_h$  of the 'pinned' model in tight-binding (TB) theory [4] are the reference levels suggested by different researchers.

Recently, we have also suggested a theoretical method [5] for  $\Delta E_v$  which took the average of the bonding energy and antibonding energy (it is called the 'average bond energy' hereafter)  $E_m$  as a reference level. In this paper, we apply this method to the  $\Delta E_v$  calculations for 16 lattice-matched heterojunctions. The results show excellent agreement with experimental data, and the accuracy is comparable with that of those of the more elaborate self-consistent supercell interface calculations by the norm-conserving pseudopotential method (SCIC) [6] and by the atomic sphere approximation (ASA) of the linear muffin-tin orbital (LMTO) method (SCSC) [7].

## 2. Method of $\Delta E_v$ calculation

In the  $\Delta E_v$  calculation of the TB 'pinned' method [4], for a heterojunction A–B, the maximum energy  $E_v$  of the valence band and the average  $sp^3$  hybrid energy  $E_h$  were

determined by TB theory. Then, the  $\Delta E_v$ -value ( $= [E_h(A) - E_v(A)] - [E_h(B) - E_v(B)]$ ) was found. Similarly, in our  $\Delta E_v$  calculation of a heterojunction A-B, first the band structures and state densities of the materials A and B are determined by the scalar relativistic LMTO method. Then, the bonding energy  $E_b$ , antibonding energy  $E_a$  and average bond energy  $E_m$  are obtained from the following equations [8, 9]:

$$E_b = \frac{1}{4N} \sum_{n=1}^4 \sum_{\mathbf{k}} E_n(\mathbf{k}) = \frac{1}{4} \int E \rho_v(E) dE \quad (1)$$

$$E_a = \frac{1}{4N} \sum_{n=5}^8 \sum_{\mathbf{k}} E_n(\mathbf{k}) = \frac{1}{4} \int E \rho_c(E) dE \quad (2)$$

$$E_m = \frac{1}{2}(E_b + E_a). \quad (3)$$

Here,  $N$  is the number of unit cells,  $E_n(\mathbf{k})$  is the energy eigenvalue and  $\rho_v(E)$  and  $\rho_c(E)$  are the total state densities of the four valence bands and the four lowest conduction bands, respectively. Finally,  $\Delta E_v$  can be expressed as

$$\Delta E_v = [E_m(A) - E_v(A)] - [E_m(B) - E_v(B)]. \quad (4)$$

It is obvious that the accuracy of this  $\Delta E_v$  calculation depends on the aligning situation of  $E_m(A)$  and  $E_m(B)$  at the heterojunction and the accuracy of the  $E_v$ - and  $(E_m - E_v)$ -values given by the band-structure and bond energy calculations. In the CNP [1, 2], DME [3] and TB 'pinned' [4] methods, a reference level ( $E_B$ ,  $E_D$  or  $E_h$ ) which aligns at heterojunctions was assumed according to the neutral solid or dielectric screening effect without a direct numerical test. In contrast with these, in the present method, the alignment of  $E_m$  at interfaces can be numerically tested by the bond energy calculation for superlattice molecular layers (this will be discussed in the next section).

The muffin-tin basis in the LMTO ASA method [10] can be written as

$$\chi_{L'}^k(\mathbf{r}) = \frac{\Phi_{ilm}(-l-1, \mathbf{r}-\mathbf{q})}{\sqrt{s_l/2}\Phi_{il(-)}} \delta_{\mathbf{q}'\mathbf{q}} - \sum_{l'm'} \frac{\Phi_{l'm'}(l', \mathbf{r}-\mathbf{q}')}{2(2l'+1)\sqrt{s_{l'}}/2\Phi_{l'l(+)}} S_{L'L}^k. \quad (5)$$

Here,  $L = q, t, l, m$  ( $q, t$  and  $l, m$  are the indices of the atomic sphere positions and the states, respectively),  $S_{L'L}^k$  is the structure constant and the rest of the notation consists of the normal potential parameters [10]. In normal LMTO calculations,  $l'm'$  and  $lm$  include s, p, d states. Here the d state is the higher partial wave (unoccupied) and the outermost d electrons of atoms are treated as core electrons. In this paper, we let these higher d partial waves fold down according to the Löwdin [11] perturbation scheme [12], i.e. we let the  $l'm'$  in the last term in equation (5) (namely the tail of the MT basis) include s, p, d states, while the  $lm$  in the MT basis includes s, p states only. We apply this treatment to two atoms in the unit cell of Si, Ge, AlP, AlAs and AlSb (the  $d_{LL}$  approach). For the materials ZnSe, ZnTe, CdTe and HgTe, we treat the outermost d electrons of the cations as valence electrons and the d electrons of anions are core electrons respectively (the  $d_{BL}$  approach). For GaAs, GaSb, InAs and InSb, both of these two approaches,  $d_{LL}$  and  $d_{BL}$ , are used.

In the calculation of  $E_m$ , we use the Chadi-Cohen special  $k$ -points for Brillouin zone summation. We found from the test calculations for GaAs that the difference between the  $(E_m - E_v)$ -values obtained from a two-special- $k$ -point and a ten-special- $k$ -point calculation is only about 0.01 eV. In this paper, we therefore adopt two special  $k$ -points. The calculated results are listed in table 1 together with the  $(E_h - E_v)$ -values of Harrison and Tersoff (the TB 'pinned' method). It can be seen that, although the  $(E_m - E_v)$ -values are obviously different from the  $(E_h - E_v)$ -values, the material dependence of these two results is perfectly consistent.

Table 1. The calculated valence band maximum energy  $E_v$ , bonding energy  $E_b$ , anti-bonding energy  $E_a$  and average bond energy  $E_m$ , together with  $E_m - E_v$  obtained by the  $d_{LL}$  and  $d_{BL}$  approaches, as well as  $E_h - E_v$  from the TB theory in [4].

| Material | $d_{LL}$ approach |               |               |               |                     | $d_{BL}$ approach |               |               |               |                     | TB                  |
|----------|-------------------|---------------|---------------|---------------|---------------------|-------------------|---------------|---------------|---------------|---------------------|---------------------|
|          | $E_b$<br>(eV)     | $E_a$<br>(eV) | $E_m$<br>(eV) | $E_v$<br>(eV) | $E_m - E_v$<br>(eV) | $E_b$<br>(eV)     | $E_a$<br>(eV) | $E_m$<br>(eV) | $E_v$<br>(eV) | $E_m - E_v$<br>(eV) | $E_h - E_v$<br>(eV) |
| Si       | -5.49             | 5.33          | -0.08         | -0.13         | 0.05                |                   |               |               |               |                     | -0.03               |
| Ge       | -6.23             | 4.31          | -0.96         | -0.57         | -0.39               |                   |               |               |               |                     | -0.32               |
| AlP      | -5.86             | 5.42          | -0.22         | -1.23         | 1.01                |                   |               |               |               |                     | 0.76                |
| AlAs     | -6.10             | 4.81          | -0.65         | -1.23         | 0.59                |                   |               |               |               |                     | 0.46                |
| AlSb     | -5.90             | 3.59          | -1.16         | -1.32         | 0.16                |                   |               |               |               |                     | 0.23                |
| GaP      | -6.23             | 5.24          | -0.49         | -1.13         | 0.64                | -6.31             | 5.24          | -0.53         | -0.98         | 0.45                | 0.66                |
| GaAs     | -6.52             | 4.39          | -1.07         | -1.30         | 0.23                | -6.59             | 4.48          | -1.05         | -1.10         | 0.05                | 0.34                |
| GaSb     | -6.21             | 3.40          | -1.41         | -1.28         | -0.13               | -6.26             | 3.52          | -1.37         | -1.09         | -0.28               | 0.14                |
| InAs     | -6.52             | 3.61          | -1.46         | -1.80         | 0.34                | -6.58             | 3.62          | -1.48         | -1.67         | 0.19                | 0.47                |
| InSb     | -6.31             | 2.72          | -1.80         | -1.87         | 0.07                | -6.37             | 2.80          | -1.80         | -1.71         | -0.09               | 0.28                |
| ZnSe     |                   |               |               |               |                     | -7.59             | 4.56          | -1.51         | -2.56         | 1.05                | 1.69                |
| ZnTe     |                   |               |               |               |                     | -6.96             | 3.62          | -1.68         | -2.29         | 0.61                | 1.40                |
| CdTe     |                   |               |               |               |                     | -7.27             | 2.83          | -2.22         | -2.90         | 0.69                | 1.43                |
| HgTe     |                   |               |               |               |                     | -7.41             | 2.78          | -2.31         | -2.62         | 0.31                |                     |

### 3. The aligning situation of $E_m$ at interfaces

In the LMTO ASA band calculation of superlattices and the bulk, it is necessary to add 'empty spheres' to the most open parts in the unit cell [13, 14]. The unit cell of  $(GaAs)_1(AlAs)_1(001)$  consists of  $(GaAs)_1$  and  $(AlAs)_1$  molecular layers. The atomic spheres and empty spheres in a  $(GaAs)_1$  or  $(AlAs)_1$  molecular layer correspond to those in a GaAs or AlAs unit cell in a one-to-one manner. We separate the ASA potentials obtained by self-consistent band-structure calculation of the  $(GaAs)_1(AlAs)_1(001)$  superlattice into two sets which correspond to  $(GaAs)_1$  and  $(AlAs)_1$  molecular layers, respectively, and use them as the input of zincblende band-structure calculations (the frozen-potential approximation). In this way, the band structures and state densities of the  $(GaAs)_1$  and  $(AlAs)_1$  molecular layers are found. Then, the  $E_b$ -,  $E_a$ - and  $E_m$ -values are obtained from equations (1), (2) and (3), respectively. Table 2 lists these results for AlAs/GaAs, AlAs/Ge and GaAs/Ge (referred to as AB/CD below).

In table 2, it can be seen for the semiconductor pair AB/CD that the  $E_m$ -values for the bulk material AB differ from those for CD. The differences  $|\Delta E_m|$

Table 2. The valence electron number  $Q_A$ ,  $Q_B$ ,  $Q_C$  and  $Q_D$  calculated by the dLL approach in the atomic layers of bulk materials AB, CD and molecular layers (AB)<sub>1</sub>, (CD)<sub>1</sub> of (AB)<sub>1</sub>(CD)<sub>1</sub> superlattices as well as the valence electron number  $Q$ , the bonding energy  $E_b$ , antibonding energy  $E_a$  and average bond energy  $E_m$  in the bulk material unit cell and in the molecular layers (AB)<sub>1</sub>, (CD)<sub>1</sub> of superlattices. The  $\Delta$  are results for AB-(AB)<sub>1</sub> and CD-(CD)<sub>1</sub>.

| AB                  | $Q_A$<br>(electrons) | $Q_B$<br>(electrons) | $Q$<br>(electrons) | $E_b$<br>(eV) | $E_a$<br>(eV) | $E_m$<br>(eV) | CD                  | $Q_C$<br>(electrons) | $Q_D$<br>(electrons) | $Q$<br>(electrons) | $E_b$<br>(eV) | $E_a$<br>(eV) | $E_m$<br>(eV) |
|---------------------|----------------------|----------------------|--------------------|---------------|---------------|---------------|---------------------|----------------------|----------------------|--------------------|---------------|---------------|---------------|
| AlAs                | 2.934                | 5.066                | 8.000              | -6.10         | 4.81          | -0.65         | GaAs                | 3.122                | 4.878                | 8.000              | -6.52         | 4.39          | -1.07         |
| (AlAs) <sub>1</sub> | 2.937                | 4.972                | 7.909              | -6.31         | 4.63          | -0.84         | (GaAs) <sub>1</sub> | 3.119                | 4.971                | 8.091              | -6.31         | 4.58          | -0.87         |
| $\Delta$            |                      |                      | -0.091             |               |               | -0.19         | $\Delta$            |                      |                      | 0.091              |               |               | 0.20          |
| AlAs                | 2.934                | 5.066                | 8.000              | -6.10         | 4.81          | -0.65         | Ge                  | 4.000                | 4.000                | 8.000              | -6.23         | 4.31          | -0.96         |
| (AlAs) <sub>1</sub> | 2.953                | 4.991                | 7.944              | -6.36         | 4.73          | -0.82         | (GeGe) <sub>1</sub> | 3.972                | 4.084                | 8.056              | -6.13         | 4.42          | -0.85         |
| $\Delta$            |                      |                      | -0.056             |               |               | -0.17         | $\Delta$            |                      |                      | 0.056              |               |               | 0.11          |
| GaAs                | 3.122                | 4.878                | 8.000              | -6.52         | 4.39          | -1.07         | Ge                  | 4.000                | 4.000                | 8.000              | -6.23         | 4.31          | -0.96         |
| (GaAs) <sub>1</sub> | 3.136                | 4.899                | 8.036              | -6.56         | 4.47          | -1.04         | (GeGe) <sub>1</sub> | 3.978                | 3.897                | 7.964              | -6.33         | 4.24          | -1.04         |
| $\Delta$            |                      |                      | 0.035              |               |               | 0.03          | $\Delta$            |                      |                      | -0.035             |               |               | -0.08         |

are 0.42 eV, 0.31 eV and 0.11 eV, respectively. However, after they constitute a monolayer superlattice, these differences between the  $(AB)_1$  and  $(CD)_1$  molecular layers become 0.03 eV, 0.03 eV and 0.00 eV. It is obvious that the  $|\Delta E_m|$ -values in the heterojunction AB/CD decrease by about an order of magnitude relative to those between individual semiconductors AB and CD. Therefore, the  $E_m$ -values are very close to aligned at the interface. The results are in agreement with the estimation in [4], i.e.  $[E_h(B) - E_h(A)]/\epsilon_\infty$  with the long-wavelength dielectric constant  $\epsilon_\infty \approx 10$ .

From the data listed in table 2, one can find that, for example, in the  $(GaAs)_1(AIAs)_1(001)$  superlattice, 0.091 electrons are transferred from the higher- $E_m$  molecular layer  $(AIAs)_1$  to the lower- $E_m$  molecular layer  $(GaAs)_1$ . Similarly, in  $(AIAs)_1(GeGe)_1(001)$  and  $(GaAs)_1(GeGe)_1(001)$ , the numbers of valence electrons transferred are 0.056 and 0.035, respectively. We can consider that the valence electron transfer between two semiconductors will cause the  $E_m$  on the two sides of the heterojunction to align at this interface.

Besides the above calculations of 1 + 1 superlattices, we have performed further supercell self-consistent calculations for the 3 + 3  $(GaAs)_3(AIAs)_3(001)$  superlattice. In terms of the resulting band structure, the average bond energy  $E_m$ , the valence band maximum  $E_v$  and the valence electron number  $Q$  in each of the three  $(GaAs)$  molecular layers and three  $(AIAs)$  molecular layers are determined. These results are given in table 3. It is shown that the excessive number  $\Delta Q$  of electrons due to interface charge transfer are almost all collected in the two interface molecular layers, namely the 3- $(GaAs)$  and 6- $(AIAs)$  layers, and the valence electron transfer is also from the molecular layer corresponding to the high- $E_m$  bulk material  $(AIAs)$  to those corresponding to the low- $E_m$  bulk material  $(GaAs)$ . The excessive electron number  $\Delta Q$  is consistent with those in the case of the 1 + 1  $(GaAs)_1(AIAs)_1(001)$  superlattice. In table 3 it can also be seen that the  $E_m$ -values in each molecular layer of the supercell are fairly close to each other. In particular, the difference between  $E_m$  for the two sets of interface molecular layers, i.e. 3- $(GaAs)$  and 4- $(AIAs)$ , and 1- $(GaAs)$  and 6- $(AIAs)$ , appears to be only 0.01 eV.

Table 3. The  $E_m$ ,  $E_v$ ,  $Q$ - and  $\Delta Q$ -values in each of the six molecular layers of the 3 + 3  $(GaAs)_3(AIAs)_3(001)$  superlattice obtained by supercell self-consistent calculations.

| Parameter<br>(units)   | Value for the following molecular layers |          |          |          |          |          |
|------------------------|--|----------|----------|----------|----------|----------|
|                        | 1-(GaAs)                                 | 2-(GaAs) | 3-(GaAs) | 4-(AIAs) | 5-(AIAs) | 6-(AIAs) |
| $E_m$ (eV)             | -0.85                                    | -0.87    | -0.89    | -0.90    | -0.88    | -0.84    |
| $E_v$ (eV)             | -1.10                                    | -1.12    | -1.12    | -1.49    | -1.48    | -1.46    |
| $Q$ (electrons)        | 7.994                                    | 7.995    | 8.092    | 8.006    | 8.005    | 7.908    |
| $\Delta Q$ (electrons) | -0.006                                   | -0.005   | 0.092    | 0.006    | 0.005    | -0.092   |

The above numerical results demonstrate directly the alignment of the  $E_m$ -level at heterojunctions. Therefore, it is reasonable to take  $E_m$  as a reference level for determining the heterojunction valence band offsets  $\Delta E_v$ .

#### 4. Results of $\Delta E_v$ and conclusions

In terms of equation (4) and the results listed in table 1, the  $\Delta E_v$ -values for 16 lattice-matched heterojunctions are obtained and shown in table 4. The data listed

in the LL column are obtained from the  $(E_m - E_v)$ -values listed in the  $d_{LL}$  column in table 1. The values given in the BL column are those for compounds containing Ga, In, Zn, Cd and Hg; the  $(E_m - E_v)$ -values are taken from the  $d_{BL}$  column in table 1, and the rest are the same as in the  $d_{LL}$  column. The results given by several 'semiempirical methods' (CNP [1, 2], DME [3] and TB 'pinned' [4]) and self-consistent interface methods (SCIC [6] and SCSC [7]) as well as the self-consistent dipole profile (SCDP) [15] method and experiments are also listed. In this section, some of the important results will be discussed.

**Table 4.** The  $\Delta E_v$ -values given by the  $d_{LL}$  and  $d_{BL}$  approaches (this work), the CNP [2] DME [3] and TB 'pinned' [4] methods in which reference levels were introduced, and the self-consistent interface calculation methods SCIC [6] and SCSC [7] as well as the CDSP method [15] in which the interface dipole effect was included, and experiments.

| Heterojunction | $\Delta E_v$ (eV) |      |                         |      |      |                      |      |             |                                    |
|----------------|-------------------|------|-------------------------|------|------|----------------------|------|-------------|------------------------------------|
|                | This work         |      | Self-consistent methods |      |      | Semiempirical models |      |             | Experiment <sup>a</sup> [7, 8, 10] |
|                | LL                | BL   | SCIC                    | SCSC | SCDP | DME                  | CNP  | TB 'pinned' |                                    |
| AlP/Si         | 0.96              | 0.96 | 1.03                    | 0.91 | 0.86 | 0.91                 | 0.91 | 0.79        |                                    |
| AlP/GaP        | 0.37              | 0.56 | 0.36                    | 0.59 | 0.59 | 0.34                 | 0.46 | 0.10        |                                    |
| AlAs/Ge        | 0.98              | 0.98 | 1.05                    | 1.03 | 1.07 | 0.84                 | 0.87 | 0.78        | 0.95*                              |
| AlAs/GaAs      | 0.36              | 0.54 | 0.37                    | 0.53 | 0.54 | 0.39                 | 0.55 | 0.12        | 0.55, 0.42                         |
| AlSb/GaSb      | 0.30              | 0.44 | 0.38                    | 0.45 |      | 0.30                 | 0.38 | 0.09        | 0.4                                |
| GaP/Si         | 0.59              | 0.40 | 0.61                    | 0.27 | 0.20 | 0.57                 | 0.45 | 0.69        | 0.80*                              |
| GaAs/Ge        | 0.62              | 0.44 | 0.63                    | 0.46 | 0.45 | 0.45                 | 0.32 | 0.66        | 0.56*                              |
| InAs/GaSb      | 0.47              | 0.47 | 0.38                    | 0.46 | 0.41 | 0.54                 | 0.43 | 0.33        | 0.51, 0.57                         |
| ZnSe/Ge        |                   | 1.44 | 2.17                    | 1.58 | 1.36 | 1.57                 | 1.52 | 2.01        | 1.52*, 1.29                        |
| ZnSe/GaAs      |                   | 1.00 | 1.59                    | 1.07 | 0.95 | 1.13                 | 1.20 | 1.35        | 1.10*, 0.96                        |
| ZnTe/GaSb      |                   | 0.89 |                         | 0.83 | 0.76 | 0.71                 | 0.77 | 1.26        | 0.34* [16]                         |
| ZnTe/InAs      |                   | 0.42 |                         | 0.31 | 0.40 |                      | 0.34 | 0.93        |                                    |
| ZnTe/AlSb      |                   | 0.45 |                         |      | 0.39 |                      | 0.39 | 1.17        |                                    |
| CdTe/InSb      |                   | 0.78 |                         | 0.93 | 0.76 | 0.73                 | 0.84 | 1.15        | 0.87*                              |
| CdTe/HgTe      |                   | 0.38 |                         | 0.22 | 0.43 | 0.61                 | 0.51 | 0.09        | 0.35, 0.12                         |
| HgTe/InSb      |                   | 0.40 |                         | 0.45 | 0.26 | 0.01                 | 0.33 |             |                                    |

<sup>a</sup> The experiments on the (110) interface are indicated with an asterisk (\*). The other experiments were on the (001) interface, except for CdTe/HgTe, which was on the (111) interface.

#### 4.1. Effects of the d state on the $\Delta E_v$ -value

From the viewpoint of the theoretical model, the present method is similar to the TB 'pinned' method of Harrison and Tersoff [4]. However, some of the important details in the calculation method are different. In fact, our results given by the LL or BL approaches (see table 4) are in excellent agreement with experimental data, whereas some of the corresponding values obtained by the TB 'pinned' method obviously deviate from the experimental values. For example, the  $\Delta E_v$ -values for the common-anion heterojunctions AlP/GaP, AlAs/GaAs, AlSb/GaSb and CdTe/HgTe are much smaller. These rather smaller  $\Delta E_v$ -values given by the TB 'pinned' method may be due to the omission of the d state in the TB calculations of  $E_v$  and  $E_h$  [16, 17]. In our LMTO ASA band-structure and bond energy calculations, we consider the hybridization of the d state with the s, p states. The resulting electronic structures

are, therefore, closer to those in real crystals and the  $E_v$ - and  $E_m$ -values obtained are more reasonable.

#### 4.2. Different treatments for the d state

We found in our calculation that the resulting  $\Delta E_v$  depends not only on the d states but on the different treatments for the d state. Table 5 gives the following results for GaAs obtained by the  $d_{LL}$  and  $d_{BL}$  approaches:  $E_v$ ,  $E_m$  and the angular momentum decomposition of the wavefunction (the s function is zero and therefore not listed) contained in the eigenstate of the valence band maximum ( $\Gamma_{15v}$ ). It can be found that, when the  $d_{LL}$  approach is replaced by the  $d_{BL}$  approach, the partial wave state constitution of the As atomic sphere remains unaltered, while the d partial wave of Ga decreases obviously. Together with these, the  $E_v$ -value increases by 0.2 eV, the  $E_m$ -value increases by 0.02 eV and  $E_m - E_v$  decreases by 0.18 eV. Similarly, in table 1, it can also be seen that, as the  $d_{LL}$  approach is substituted for with the  $d_{BL}$  approach, the  $(E_m - E_v)$ -values for GaP, GaAs, GaSb, InAs and InSb decrease by 0.15–0.19 eV. Therefore, in table 4, for AlP/GaP, AlAs/GaAs and AlSb/GaSb the  $\Delta E_v$ -values (given by equation (4)) from the BL approach are larger than those from the LL approach while for GaP/Si and GaAs/Ge the BL results are smaller than the LL results

Table 5. The calculated results for  $E_m$ ,  $E_v$  and angular momentum decomposition of the wavefunction at valence maximum  $\Gamma_{15v}$ , for GaAs.

|          | $E_v$<br>(eV) | $E_m$<br>(eV) | Ga sphere |      | As sphere |      |
|----------|---------------|---------------|-----------|------|-----------|------|
|          |               |               | p         | d    | p         | d    |
| $d_{LL}$ | -1.30         | -1.07         | 0.13      | 0.09 | 0.69      | 0.01 |
| $d_{BL}$ | -1.10         | -1.05         | 0.16      | 0.05 | 0.69      | 0.01 |

#### 4.3. Comparison with other models

Recently, Lambrecht *et al* presented three theoretical models, i.e. the SCDP model [15], the self-consistent dipole model [18] and the interface-bond-polarity model [19], in which the interface dipole effect associated with interface charge transfer is investigated in detail. Their work showed that the interface dipole and dielectric screening play important roles in the energy band line-up. In several non-interface self-consistent models, e.g. the CNP, DME and TB 'pinned' models, the alignment of the reference levels  $E_B$ ,  $E_D$  or  $E_h$  at interfaces is inferred from the interface dipole role or the dielectric screening effect without further strong numerical evidence. They did not demonstrate further the important role of interface charge transfer or interface dipole in detail. The present work is also a model with reference level alignment, but we perform a direct numerical test by investigating the relation between the interface charge transfer and the alignment of the average bond energy  $E_m$ . Our results demonstrate the important role of interface charge transfer in energy band line-up. The interface charge  $\Delta q$  introduced in the dipole model [15, 18, 19] which determines the interface dipole simply corresponds to the transferred interface charge  $\Delta Q$  in the present model which causes  $E_m$  to align at interfaces. Both of these two models focus on the interface charge transfer. They differ in that, in the dipole



model, the role of charge transfer acting on energy band alignment is displayed by the charge-transfer-induced dipole whereas, in our model, it is shown by the charge-transfer-induced  $E_m$ -shift. The present method requires only calculations of the bulk material band structure and average bond energy  $E_m$ ; thus, it is more convenient than the dipole model for which the interface dipole calculations are required.

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