The empirical pseudopotential method in the calculation of heterostructure band offsets

The empirical pseudopotential method in the calculation of heterostructure band offsets

Yong-Mei Zheng†, Ren-Zhi Wang†‡ and Yi-Bai Li†§

† Physics Department, Xiamen University, Xiamen, 361005, People's Republic of China
‡ CCAST (World Laboratory), PO Box 8730, Beijing, 100080, People's Republic of China

Abstract. The empirical pseudopotential method, with the average bond energy E_m as the energy reference, is applied for the first time in the calculation of band offsets in semiconductor heterostructures. The calculations are carried out for three heterostructures: GaAs/Ge, AlAs/GaAs and AlAs/Ge. A picture of the band structures and their alignments, including conduction bands and valence bands, is given. The calculated valence band offsets are 0.57 eV for GaAs/Ge, 0.50 eV for AlAs/GaAs, and 1.07 eV for AlAs/Ge, in excellent agreement with experimental data.

1. Introduction

The empirical nonlocal pseudopotential method (ENPM) [1] is widely used in calculating the band structure, and optical and electrical properties of bulk semiconductor materials. However, this method has not been used in the calculation of band alignment of heterostructures. In order to determine the band alignment of A/B heterostructures, it is necessary to employ the same energy reference for A and B materials. In some first-principles calculations, the atomic potential of various materials at infinity is taken as the zero to which the energy is referred; therefore the valence band offset ΔE_v of the heterostructures can be calculated conveniently [2–6]. However, in the ENPM band calculation, the choice of energy reference can be arbitrary (it can change with the value of the average lattice potential $V(0)$), and no absolute energy reference is available. The calculated results for band structures are usually referred to the valence band maximum (VBM) as the zero (the VBM is set at '0' for various materials). Thus in order to apply the ENPM in studying band alignment of A/B heterostructures, it is necessary to propose a suitable energy reference and to determine relevant band parameters.

In our previous papers [7, 8], the linear muffin-tin orbital (LMTO) method was used in calculating heterostructure band alignment. It was suggested that one could calculate the average bonding energy E_m with the band structure $E_n(\boldsymbol{k})$ calculated using the first-principles method:

$$E_m = \frac{1}{8} \sum_{n=1}^{8} \sum_{k} E_n(\boldsymbol{k}). \tag{1}$$

Although the average bonding energy E_m differs among various bulk materials, it was found in our previous studies [7, 8] that the average bonding energies $E_m(A)$ and $E_m(B)$ show

§ Present address: Physics Department, University of Sheffield, Sheffield S3 7RH, UK.

'self-alignment' behaviour in A/B heterostructures, i.e. the E_m-values are very close to each other across the interface. This behaviour was explained in terms of the transfer of valence electrons between two constituting materials which leads to the formation of the dipoles; the energy potentials contributed by the interface dipoles compensate the difference between the E_m-values across the interface [7, 8]. The average bonding energy E_m is similar to: the charge neutrality point E_B proposed by Tersoff [9, 10]; the average hybrid energy E_h used by Harrison and Tersoff [11]; and the dielectric midpoint energy E_D introduced by Cardona and Christensen [3]; all of these energies show 'self-alignment' behaviour and each can be used as the energy reference for calculating the valence band offset. 'Self-alignment' of E_B, E_h and E_D was assumed according to the neutral-solid or the dielectric screening effect [3, 9–11]; however, the 'self-alignment' of E_m can be tested numerically by performing a bond energy calculation for the superlattice molecular layers [8].

The energy difference ($E_v^m = E_m - E_v$) between the valence band maximum E_v and the average bonding energy E_m is an important parameter in determining the valence band offset. Based on the 'self-alignment' behaviour of E_m, a method (called the average-bond-energy method) was proposed for calculating the valence band offset of A/B heterostructures [7, 8, 12–14]:

$$\Delta E_v = [E_m(A) - E_v(A)] - [E_m(B) - E_v(B)]. \tag{2}$$

It can be seen from equation (1) that the average bonding energy E_m is determined by the band structure $E_n(\boldsymbol{k})$ which is independent of the band calculation method. And the band parameter E_v^m ($=E_m - E_v$) in equation (2) is also independent of the energy reference used in the band calculation. Therefore the average-bond-energy method can be used in combination with different band calculation methods, including the ENPM.

The first-principles band calculation based on the local density approximation has so far only been able to provide the accurate structure of the valence band, and not those of the conduction band and band gap which are related to the excited states (tending to give a smaller band gap). The average-bond-energy method based on the LMTO band calculation is only suitable for calculating the valence band offset ΔE_v, and not for directly calculating ΔE_g and ΔE_c. However, the quasiparticle method (GWA) [15, 16] and the ENPM [1] are two available methods for calculating accurately the valence band, conduction band and band gap simultaneously. The quasiparticle method is very complicated and involves enormous computing effort; this method is unsuitable for a wide range of applications. However, the combination of the ENPM with the average-bond-energy method can not only enable one to calculate accurately ΔE_v, ΔE_c and ΔE_g in heterostructures, but also reduce greatly the amount of calculation involved. Our method is applied for the first time to calculate the band alignment in three heterostructures: GaAs/Ge, AlAs/GaAs and AlAs/Ge. It is shown that the relatively simple method, which requires limited computing effort, can provide accurately an overall picture of band alignment in heterostructures. Our calculation results are in good agreement with experimental data.

2. Calculation method and results

The band structure $E_n(\boldsymbol{k})$ in the ENPM is given by the solution of the following secular equation:

$$\det\left|H_{ij}(\boldsymbol{k}) - E_n(\boldsymbol{k})\delta_{ij}\right| = 0 \tag{3}$$

where i and j are the indices of the plane-wave basis of wavevectors $\boldsymbol{k}_i = \boldsymbol{k} + \boldsymbol{K}_i$ and $\boldsymbol{k}_j = \boldsymbol{k} + \boldsymbol{K}_j$, $\boldsymbol{K}_i$ and $\boldsymbol{K}_j$ are the reciprocal-lattice vectors, and $\boldsymbol{G} = \boldsymbol{k}_j - \boldsymbol{k}_i$ is the reciprocal-

Table 1. Pseudopotential parameters for Ge, GaAs and AlAs.

| | Local pseudopotential parameters (Ryd) | | | | | | Nonlocal pseudopotential parameters (au) | | | |
| | Symmetry | | | Anti-symmetry | | | A atom (Cation) | | B atom (Anion) | |
	$V_s(\sqrt{3})$	$V_s(\sqrt{8})$	$V_s(\sqrt{11})$	$V_a(\sqrt{3})$	$V_a(\sqrt{4})$	$V_a(\sqrt{11})$	R_1	A_2^1	R_2	A_2^2
Ge	−0.233	0.017	0.059	0.000	0.000	0.000	2.200	0.275	2.200	0.275
GaAs	−0.226	0.015	0.067	0.057	0.052	0.000	2.350	0.225	2.050	0.675
AlAs	−0.216	0.049	0.060	0.071	0.070	−0.001	2.350	0.020	2.050	0.625

Table 2. Eigenvalues for Ge at Γ, X and L (in eV).

Ge	This paper	ENPM [1]	GWA [16]	Experiment†
Γ_{1v}	−12.57	−12.66	−12.84	−12.6 ± 0.2, 12.9 ± 0.2
Γ'_{25v}	0.00	0.00	0.00	0.00
Γ'_{2c}	0.89	0.90	0.65	0.89
Γ_{15c}	3.22	3.01	3.21	3.01, 3.21
X_{1v}	−8.77	−8.65	−9.06	−9.3 ± 0.2
X_{4v}	−3.14	−3.29	−3.16	−3.15 ± 0.2, −3.5 ± 0.2
X_{1c}	1.30	1.16	1.74	1.3 ± 0.2
L_{2v}	−10.49	−10.39	−10.82	−10.6 ± 0.5
L_{1v}	−7.53	−7.67	−7.81	−7.7 ± 0.2
L_{3v}	−1.44	−1.43	−1.47	−1.4 ± 0.3
L_{1c}	0.74	0.76	0.98	0.744
L_{3c}	4.33	4.16	4.57	4.3 ± 0.2, 4.2 ± 0.1
L_{2c}	7.66		9.20	7.8 ± 0.6, 7.9 ± 0.1
E_m	−0.36			

† Quoted from reference [16].

lattice vector related to $\boldsymbol{k}_i$ and $\boldsymbol{k}_j$. H_{ij} is composed of 'local' H_{ij}^L and 'non-local' H_{ij}^N parts, i.e.

$$H_{ij} = H_{ij}^L + H_{ij}^N.$$

Here

$$H_{ij}^L = \frac{\hbar^2}{2m}(\boldsymbol{k} + \boldsymbol{K}_i)^2 \delta_{ij} + V(\boldsymbol{G}) \tag{4}$$

where

$$V(\boldsymbol{G}) = V_S(\boldsymbol{G})\cos(\boldsymbol{G} \cdot \boldsymbol{\tau}) + iV_A(\boldsymbol{G})\sin(\boldsymbol{G} \cdot \boldsymbol{\tau})$$
$$\boldsymbol{\tau} = \frac{a}{8}(1, 1, 1)$$

where a is the lattice constant, and $V_S(\boldsymbol{G})$ and $V_A(\boldsymbol{G})$ are the symmetric and the anti-symmetric form factors of the pseudopotential, respectively. Also,

$$H_{ij}^N = \frac{4\pi}{\Omega} \sum_l (2l + 1) P_l(\cos\theta_{ij}) \sum_t A_l^t F_l^t(k_i, k_j) \exp(i\boldsymbol{G} \cdot \boldsymbol{\tau}_t) \tag{5}$$

Table 3. Eigenvalues for GaAs and AlAs at Γ, X and L (in eV).

	GaAs				AlAs	
	This paper	ENPM [1]	GWA [16]	Experiment†	This paper	Experiment‡
Γ_{1v}	−12.50	−12.55	−12.69	−13.21	−11.87	
Γ_{15v}	0.00	0.00	0.00	0.00	0.00	
Γ_{1c}	1.52	1.51	1.32	1.52	3.18	3.13
Γ_{15c}	4.57	4.55	4.60	4.61	5.07	
X_{1v}	−10.25	−9.83	−10.27	−10.86	−9.72	
X_{3v}	−6.68	−6.88	−7.16	−6.81	−5.75	
X_{5v}	−2.79	−2.89	−2.71	−2.91	−2.50	−2.41
X_{1c}	1.90	2.03	2.65	1.90	2.23	2.23
X_{5c}	2.51	2.38	2.72	2.47	3.13	2.99
L_{1v}	−10.89	−10.60	−10.02	−11.35	−10.34	
L_{1v}	−6.59	−6.83	−6.91	−6.81	−5.89	
L_{3v}	−1.19	−1.42	−1.17	−1.41	−0.97	−1.12
L_{1c}	1.74	1.82	1.92	1.74	3.05	3.03
L_{3c}	5.53	5.47	5.65	5.45	5.42	
L_{1c}	8.01		9.92	8.6	8.82	
E_m	0.21				0.71	

† Quoted from reference [16].
‡ Quoted from reference [18].

where

$$F_l^t(k_i, k_j) = \begin{cases} (1/2R^2)\{[J_l(k_i R)]^2 - J_{l-1}(k_i R) J_{l+1}(k_i R)\} & k_i = k_j \\ [R^2/(k_i^2 - k_j^2)][k_i J_{l+1}(k_i R) J_l(k_j R) - k_j J_{l+1}(k_j R) J_l(k_i R)] & k_i \neq k_j \end{cases}$$

where Ω is the volume of the unit cell, l is the angular momentum quantum number, $k_i = |\boldsymbol{k}_i|$ and $k_j = |\boldsymbol{k}_j|$, $\boldsymbol{\tau}_t$ is the position vector of the tth atom in the unit cell, P_l are the Legendre polynomials, θ_{ij} is the angle between $\boldsymbol{k}_i$ and $\boldsymbol{k}_j$, A_l^t is the pseudopotential well depth of the tth atom, R is the core radius of the pseudopotential of the tth atom (R_t), and J_l are the spherical Bessel functions.

Table 4. Parameters of band alignments in Ge, GaAs and AlAs (in eV).

	Ge	GaAs	AlAs
$E_m - E_v(\Gamma)$	−0.36	0.21	0.71
$E_m - E_c(\Gamma)$	−1.25	−1.31	−2.47
$E_m - E_c(X)$	−1.66	−1.69	−1.52
$E_m - E_c(L)$	−1.10	−1.53	−2.34

As in reference [1], only nonlocal corrections of d states ($l = 2$) were included in our ENPM calculations of Ge, GaAs and AlAs. The upper kinetic energy cut-off of the plane-wave basis was selected as 8.0 Ryd. Because the three materials form heterostructures with good lattice matching, the lattice constant was taken as 5.65 Å for the three materials. With the continuous improvements in experimental techniques, up-to-date experimental data

Table 5. Conduction and valence band offsets for three heterostructures (in eV).

	GaAs/Ge	AlAs/Ge	AlAs/GaAs
$\Delta E_v(\Gamma/\Gamma)$	0.57	1.07	0.50
$\Delta E_c(\Gamma/\Gamma)$	0.06	1.22	1.16
$\Delta E_c(X/\Gamma)$	0.44	0.27	0.21†
$\Delta E_c(L/\Gamma)$	0.28	1.09	1.03
$\Delta E_c(\Gamma/X)$	−0.35	0.81	0.94
$\Delta E_c(X/X)$	0.03	−0.14	−0.01
$\Delta E_c(L/X)$	−0.13	0.68	0.81
$\Delta E_c(\Gamma/L)$	0.21†	1.37	0.78
$\Delta E_c(X/L)$	0.59	0.42†	−0.17
$\Delta E_c(L/L)$	0.43	1.24	0.65

† The lowest conduction band offset.

show considerable differences from the old data quoted in the previous ENPM calculation [1]. Therefore the form factors of the local pseudopotentials $V_S(G)$ and $V_A(G)$ ($G = |\boldsymbol{G}|$), the well depth A_l^t of the nonlocal pseudopotential, and the core radius R_t were adjusted in our ENPM calculation, in order to obtain the best match of the direct and indirect band gaps with up-to-data experimental data for Ge, GaAs and AlAs. The pseudopotential parameters used in our calculations are given in table 1. Tables 2 and 3 give the calculated eigenvalues for Ge, GaAs, and AlAs at the Γ, X, and L points, which are compared with those from previous ENPM calculations [1], and the quasiparticle method (GWA) [16], and up-to-data experimental data. In order to calculate the average bond energies E_m of Ge, GaAs and AlAs, the band structures $E_n(\boldsymbol{k})$ at the 10 special k-points in the Brillouin zone [17] were calculated first, then four valence bands and the four lowest conduction bands were included in the calculation of E_m (cf. equation (1)). Because the spin–orbit splittings in the valence band are very close for GaAs (0.34 eV), Ge (0.30 eV) and AlAs (0.29 eV), the effect of the spin–orbit splitting on the valence band offset is estimated to be <0.02 eV. Therefore it is reasonable to neglect the spin–orbit-splitting effect in our calculation. The calculated E_m-values are also listed in tables 2 and 3.

Table 4 gives the band parameters $E_m - E_v$ and $E_m - E_c$, calculated according to the valence band maxima, conduction band minima and average bond energies E_m given in tables 2 and 3. The conduction band offsets and valence band offsets of GaAs/Ge, AlAs/Ge and AlAs/GaAs heterostructures are given in table 5; these were determined according to the 'self-alignment' behaviour of the average bond energy E_m. Figure 1 shows the calculated band alignments of the valence bands, conduction bands, direct gaps and indirect gaps of GaAs/Ge, AlAs/Ge and AlAs/GaAs heterostructures.

3. Discussion and conclusion

The relationship among the valence band offset ΔE_v, conduction band offset ΔE_c and band gap shift ΔE_g in an A/B heterostructure is given by

$$\Delta E_v + \Delta E_c = \Delta E_g \tag{6}$$

where
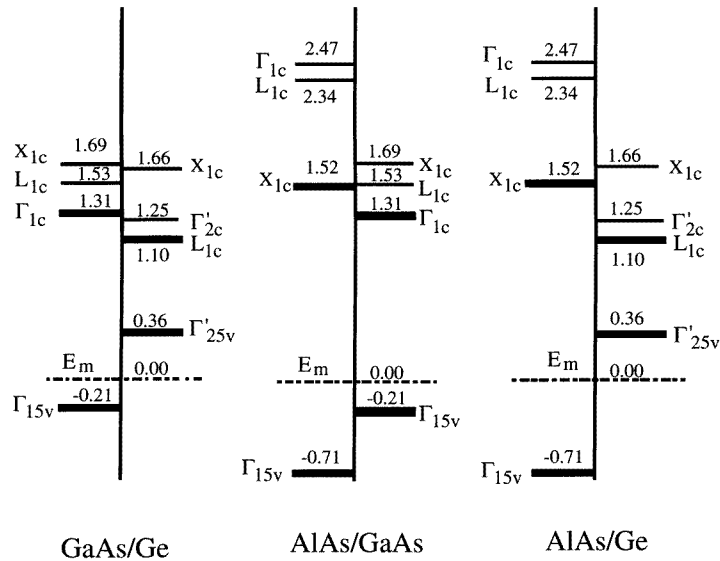
$$\Delta E_g = E_g(A) - E_g(B).$$

Figure 1. A schematic diagram of the alignment of the conduction bands and valence bands in GaAs/Ge, AlAs/Ge and AlAs/GaAs heterostructures (in eV).

Table 6. A comparison of calculated valence band offsets and experimental data (in eV).

	This paper	SCSC [2]	SCIC [4]	Experimental data
GaAs/Ge	0.57	0.46	0.63	0.53[a], 0.56[b], 0.60[c]
AlAs/GaAs	0.50	0.53	0.37	0.42[d], 0.45[e], 0.55[f]
AlAs/Ge	1.07	1.03	1.05	0.95[g]

[a] Reference [19].
[b] Reference [20].
[c] Reference [21].
[d] Reference [22].
[e] Reference [23].
[f] Reference [24].
[g] Reference [25].

The accuracy of ΔE_g is determined by the accuracy in calculating $E_g(A)$ and $E_g(B)$ for the individual materials. As seen from tables 1 and 2, the band gaps E_g (direct and indirect) of Ge, GaAs and AlAs, which are calculated with our ENPM, agree well with the experimental data. Therefore the accuracy of ΔE_c (as seen in equation (6)) depends mainly on the accuracy in calculating ΔE_v with the average-bond-energy method. The calculated accuracy of ΔE_v is tested in table 6, by comparing with the corresponding value calculated with the more elaborate self-consistent supercell interface calculation SCSC [2] and SCIC [4] methods, and with experimental data.

As seen from table 6, the valence band offsets ΔE_v of our calculations for GaAs/Ge and AlAs/GaAs heterostructures lie between the values which were given by the SCSC and SCIC calculations, and are close to the average of the different experimental values. Therefore our calculation results are clearly reasonable and reliable. There are few valence band offsets ΔE_v measured for the AlAs/Ge heterostructures; no reliable comparison can

be made between theoretical values and experimental data. However, our value is close to those given by the SCSC and SCIC methods. The ΔE_v-values obtained by us for these lattice-matched heterostructures are also close to the values calculated by Jaros [26] (his analytic model gives only $\Delta E_v(\Gamma/\Gamma)$). A very limited number of conduction band offsets ΔE_c have been reported experimentally for the three heterostructures discussed above; the conduction band offsets of the AlAs/GaAs heterostructure found in reference [27] are $\Delta E_c(X/\Gamma) = 0.2$ eV and $\Delta E_c(L/\Gamma) = 1.0$ eV. The *ab initio* pseudopotential calculation [28] gave $\Delta E_c(X/\Gamma) = 0.35$ eV and $\Delta E_c(L/\Gamma) = 1.08$ eV. Our values, $\Delta E_c(X/\Gamma) = 0.21$ eV and $\Delta E_c(L/\Gamma) = 1.03$ eV, match better with experimental data.

In summary, it is shown clearly in the above discussions that the average bond energy E_m can be used as the energy reference in pseudopotential band calculations for determining band alignment in heterostructures. The combination of the average-bond-energy method and the pseudopotential band calculation method can enable one to determine accurately conduction bands, valence bands and band gaps, and provide an overall picture of band alignments in semiconductor heterostructures.

Acknowledgments

References

[1] Chelikowsky J R and Cohen M L 1976 *Phys. Rev.* B **14** 556
[2] Christensen N E 1988 *Phys. Rev.* B **37** 4528
[3] Cardona M and Christensen N E 1987 *Phys. Rev.* B **35** 6182
[4] Van de Walle C G and Martin R M 1987 *Phys. Rev.* B **35** 8154
[5] Massidda S, Min B I and Freeman A J 1987 *Phys. Rev.* B **35** 9871
[6] Lambrecht W R L, Segall B and Andersen O K 1990 *Phys. Rev.* B **41** 2813
[7] Ke S H, Wang R Z and Huang M C 1994 *Phys. Rev.* B **49** 10 495
[8] Wang R Z, Ke S H and Huang M C 1992 *J. Phys.: Condens. Matter* **4** 8083
[9] Tersoff J 1984 *Phys. Rev.* B **30** 4874
[10] Tersoff J 1986 *Surf. Sci.* **168** 275
[11] Harrison W A and Tersoff J 1986 *J. Vac. Sci. Technol.* B **4** 1068
[12] Wang R Z and Huang M C 1991 *Acta Phys. Sinica* **40** 1683; 1992 *Chinese J. Semicond.* **13** 253 (in Chinese)
[13] Wang R Z, Huang M C and Ke S H 1993 *Sci. China* A **36** 319
[14] Wang R Z, Ke S H and Huang M C 1995 *Phys. Rev.* B **51** 1935
[15] Hedin L 1965 *Phys. Rev.* **139** 796
[16] Rohlfing M, Kruger P and Pollmann J 1993 *Phys. Rev.* B **48** 17 791
[17] Chadi D J and Cohen M L 1973 *Phys. Rev.* B **8** 5747
[18] Wei S H and Zunger A 1989 *Phys. Rev.* B **39** 3279
[19] Kraut E A, Grant R W, Waldrop T R and Kowalczyk S P 1980 *Phys. Rev. Lett.* **44** 1620
[20] Waldrop J R, Kraut E A, Kawalczyk S P and Grant K W 1983 *Surf. Sci.* **132** 513
[21] Chambers S A and Irwin T J 1988 *Phys. Rev.* B **38** 7484
[22] Menendez J, Pinczuk A, Werder D J, Gossard A C and English J H 1986 *Phys. Rev.* B **33** 8863
[23] Yu E T, Chow D H and MaGill T C 1988 *Phys. Rev.* B **38** 12 764
[24] Batey J and Wright S L 1986 *J. Appl. Phys.* **59** 1200
[25] Margaritondo C 1985 *Phys. Rev.* B **31** 2526
[26] Jaros M 1988 *Phys. Rev.* B **37** 7112
[27] Luo L F, Beresford R and Wang W I 1988 *Appl. Phys. Lett.* **53** 2320
[28] Nelson J S, Wright A F and Fong C Y 1991 *Phys. Rev.* B **43** 4908