

## Theoretical approach to heterojunction valence-band discontinuities: Case of a common anion

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Band offsets for the (100), (110), (111), and  $(\bar{1}\bar{1}\bar{1})$  orientations of the GaAs/AlAs heterojunction are calculated in a tight-binding approach. A charge-neutrality condition is used. Some face-orientation dependence is obtained: the offset of the (110) interface (0.63 eV) is different from those of polar interfaces (0.49, 0.51, and 0.47 eV). This result differs from some other recent calculations and the origin of this difference is discussed. The predicted (100) offset is in good agreement with recent experiments. The potential barrier appears to be not exactly abrupt but extends over a few planes. This effect will be very important in the case of superlattices made from very thin layers. The HgTe/CdTe heterojunction is also considered. The extension to heterojunctions with no common anion is finally discussed.

### I. INTRODUCTION

In recent years, the determination of band lineups at semiconductor heterojunctions has been the subject of intense activity, especially for the GaAs/AlAs system which has been the subject of many experiments.<sup>1-6</sup> From a theoretical point of view, band offsets can be treated by two types of approach: (i) simplified theories ranging from empirical to model calculations whose aim is to describe trends in families of compounds and, particularly, to predict band discontinuities (Refs. 7-9 and references therein); (ii) more elaborate theories that calculate the local electronic structure of the interface and allow the determination of the band offset. To obtain the interface electronic structure one can use either first-principles calculations, based on local density plus pseudopotentials (Ref. 10 and references therein), or tight-binding Green's-function calculations.<sup>11-13</sup> This last method provides a much simpler calculational tool than first-principles theories. We apply it, with a local-charge-neutrality condition to (100), (110), (111), and  $(\bar{1}\bar{1}\bar{1})$  GaAs/AlAs systems. In Sec. II we report the principle of the calculation. In particular, we show that some lack of precision in calculating densities of states can lead to large errors in the resulting offsets. We also point out the crucial importance of a proper choice of the interface coupling parameters. Our predicted offsets are given in Sec. III and compared to other theoretical calculations and experimental data. Application to CdTe/HgTe systems is also performed. In Sec. IV we discuss possible extensions of this work and conclude that the calculation described here can be directly applied to heterojunctions with a common anion.

### II. THEORY

In this section we first discuss how to describe an ideal interface configuration in a tight-binding framework. Secondly we present the self-consistent method to get band offsets and show how it can be simplified through

the use of a local-neutrality condition. Then we point out that this problem is highly sensitive to the charge numerical accuracy. We then give the numerical method we have used to calculate densities of states with the desired precision.

#### A. Tight-binding parameters

We describe the semiconductor band structures of bulk GaAs and AlAs by means of a tight-binding model using a  $sp^3s^*$  basis set.<sup>14</sup> We have reported in Appendix A the parameters used. This fit determines all the bulk tight-binding matrix elements except for the intra-atomic terms which are all determined to an unknown additive constant within each separate material. For the heterojunction, we choose as central unknown  $\Delta E_v$ , the discontinuity between the top of the valence band of the two bulk materials. We only consider ideal heterojunctions where, on both sides of the interface, atoms are distributed as in the bulk (we exclude any atomic reconstruction or relaxation near the interface). As we use a nearest-neighbor two-center approximation, the only tight-binding elements which, in the heterojunction case, differ from the bulk, are those involving atoms belonging to both interface planes. We have to consider interatomic terms (connecting the two interface planes) and intra-atomic terms.

When the two semiconductors forming the heterojunction have a common anion, interface cations have the same first neighbors as in the bulk. This allows to us approximate interactions between interface planes, e.g., between the cation of semiconductor 1 ( $C_1$ ) and the anion of semiconductor 2 ( $A_2$ ) by bulk interactions, i.e.,

$$\begin{aligned} C_1 A_2 &\equiv C_1 A_1, \\ C_2 A_1 &\equiv C_2 A_2. \end{aligned} \quad (1)$$

This rule is quite unambiguous here because we have a description involving only nearest-neighbor interactions in a two-center approximation. However, when there is no

common anion several different situations can occur. The simplest one corresponds to heterojunctions between semiconductors of the same class (i.e., IV, III-V, or II-VI). If the bonds  $C_1A_2$  and  $C_2A_1$  correspond to a known bulk material then the interactions between interface planes can be taken equal to the bulk nearest-neighbor interactions of these materials. In other cases it has been common practice to write<sup>11-13</sup>

$$\begin{aligned} C_1A_2 &= \frac{1}{2}(C_1A_1 + C_2A_2), \\ C_2A_1 &= \frac{1}{2}(C_1A_1 + C_2A_2). \end{aligned} \quad (2)$$

We first notice that this empirical rule does not lead to the correct value given by (1) in the common-anion case. It is thus important to estimate how this approximation can influence the resulting offset. For this we have applied Eq. (2) to the case of the GaAs/AlAs (110) heterojunction. We will show in Sec. III that this produces a  $\Delta E_v$  quite different from that obtained with Eq. (1). This can be explained simply in terms of charge transfers (see Sec. III).

There is also a difficulty concerning the intra-atomic terms. As usual, we first consider that the effect of the Coulomb interactions is simply to shift all levels of a given atom by the same amount (this is detailed in the next paragraph). The difficulty is then to find a coherent rule for determining the differences in such intra-atomic terms. These should not only be functions of the nature of the atom but also of its nearest neighbors. As a consequence, even in the case of a common anion we have at our disposal two sets of values for the anion. The natural method in such a case is then to take for the interface anions a weighted average of the two bulk values, the weight being fixed by the nature of the four nearest neighbors and being different at the (100) and the (110) or (111) interfaces. This reduces to a simple arithmetical average in the (100) case (see Fig. 1). We have studied the influence of these parameters on the predicted offsets and found it to be small. For instance, in the (111) case, the change in offset obtained by replacing average parameters by bulk values is of the order of 5 meV.

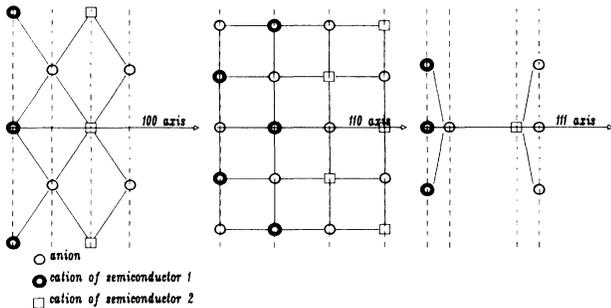


FIG. 1. Schematic representation of atomic distribution at (100), (110), and (111) heterojunctions. Dashed lines represent atomic planes parallel to the interface plane.

## B. Self-consistent procedure

Let us now describe how we take into account the existence of interface dipoles. The perturbation due to interface formation leads to some charge transfer across the interface plane. This one is responsible for the dipole potential barrier that is, in principle, essential for determining  $\Delta E_v$ . The charge disturbance will be limited only to a few planes on each side of the interface. This is due to the fact that in the materials considered here, the typical screening length of the perturbation potential due to neutral defects is of the order of 2 Å.<sup>15</sup> Such a charge transfer induces a change in the Coulomb potential and the problem has to be solved in a self-consistent way. As usual in charge-dependent tight-binding calculations, we consider that this effect only affects the diagonal matrix elements of the Hamiltonian. This means that on each plane  $i,n$  parallel to the interface (where  $i=1$  or 2 represents the material and  $n=1-\infty$  numbers the plane position away from the interface) the diagonal terms will be shifted by a quantity  $U_{in}$  from their value in the corresponding bulk material. The unknowns of the problem are thus  $\Delta E_v$  and all  $U_{in}$  (with the boundary conditions  $U_{in} \rightarrow 0$  when  $n \rightarrow \infty$ ). As they originate from Coulomb potentials they can be expressed linearly in terms of the excess charge  $\delta q_{in}$  of each plane. In turn, these charges can be calculated as functions of  $\Delta E_v$  and the  $U_{in}$  and the whole calculation has to be iterated to self-consistency. In fact, screening in such systems with high dielectric constant is very efficient, and we have shown in earlier work<sup>13</sup> that a very good approximation to the fully self-consistent solution is provided by the assumption of "local charge neutrality." This approximation has also been discussed by other authors<sup>16</sup> in terms of the dielectric constant  $\epsilon_\infty$ . In Appendix C we show that it is a rather good approximation if the tops of the bulk semiconductor valence bands are not too different. This means that one can determine  $\Delta E_v$  and the  $U_{in}$  by imposing that all  $\delta q_{in}$  be zero for a (110) heterojunction. For a polar heterojunction this "local-charge-neutrality" condition is extended to a charge distribution which preserves the electrostatic stability of the system, i.e., prevents the potential from becoming infinite far from the interface.<sup>17</sup> The general conditions for this stability have been studied for the polar surfaces of compounds.<sup>18</sup> The electrostatic stability of the system can be settled by many ways. We have chosen here the solution where only one plane (the interface anion plane) presents a charge which is different from the bulk charge. Then this charge is fixed by the electrostatic stability condition and must be equal to  $-(q_1 + q_2)/2$  for the (100) interface if  $-q_1$  and  $-q_2$  are the anion net charges in each bulk material. Again we have assumed that this charge is localized on the anion interface plane since screening occurs on very short distances.

Obviously, if  $q_1$  and  $q_2$  are equal, the local-charge-neutrality condition corresponds to the exact self-consistent solution. In our tight-binding framework, with parameters defined in Appendix A, we have, for HgTe/CdTe,  $q_1 = -0.124$  e/atom and  $q_2 = -0.269$  e/atom and, for the GaAs/AlAs system,  $q_1 = 0.178$  e/atom and  $q_2 = 0.394$  e/atom. Then, as  $q_1$  and  $q_2$  are in the same range but different, the good quality of our ap-

proximation is mainly due to strong screening, that is, to a large value of  $\chi/C$  defined in Appendix C. A more detailed discussion of the self-consistency condition for (100) heterojunctions or quantum wells will be the object of a forthcoming publication.

The application of the local-neutrality condition to determine the perturbation potentials  $U_{in}$  is relatively easy. We only write charge conditions (as defined in Fig. 2) for a finite number of planes  $N$  near the interface.  $N$  has to be high enough to provide  $\Delta E_v$  with a precision of the order of 0.01 eV. In practice we find that  $N=5$  is large enough (the difference between  $\Delta E_v$  obtained with  $N=5$  and  $N=7$  is much lower than 0.01 eV). For polar interfaces we consider the common-anion plane and two planes on each side. For nonpolar interfaces we consider three planes on one side, and two on the other side. We have checked that interchanging the two sides does not alter the solution appreciably. We then have five equations to solve and five unknowns to determine. These unknowns are  $\Delta E_v$  and four intraplane potentials  $U_{in}$ . A central issue of this problem is that if the desired precision on  $\Delta E_v$  is a few hundredths of an eV, then one has to calculate the  $\delta q_{in}$  to better than  $0.001e$ . This is simply understandable from the fact that the susceptibility (i.e., the ratio  $\Delta q/\Delta U$ ) for bonds across the interface plane is of order of a few tenths per volt. Appendix B relates the procedure used to reach this precision.

In this section we have then described how a tight-binding calculation can provide charges on each plane parallel to the heterojunction. We have also shown how the interface induces charge transfers that imply a change in the Coulomb potential. The problem has to be solved self-consistently. Muñoz *et al.*<sup>11,12</sup> have proposed recently an approximate self-consistent treatment (where Madelung terms are averaged on planes parallel to interface). In the present work we have chosen to use the approximate charge-neutrality condition which is, for the semiconductors under study, very close to the exact solution (see Appendix C). The purpose of the next section is to provide and discuss the band offsets resulting from the calculation we have just described in the case of GaAs/AlAs and CdTe/HgTe heterojunctions. We also give the potential shape for different orientations.

### III. GaAs/AlAs AND HgTe/CdTe BAND OFFSETS AND POTENTIAL SHAPE

#### A. GaAs/AlAs systems

We consider four different orientations (100), (110), (111), and  $(\bar{1}\bar{1}\bar{1})$ , the difference between (111) and  $(\bar{1}\bar{1}\bar{1})$

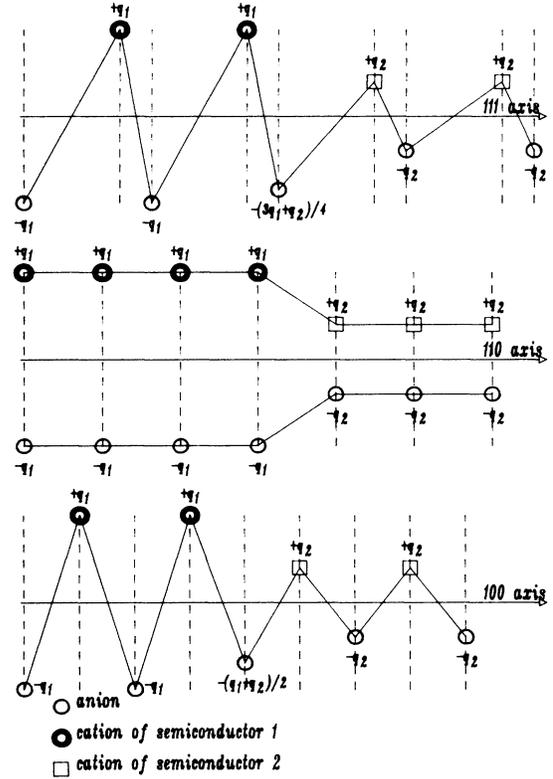


FIG. 2. Charge distribution preserving electrostatic stability of (100), (110), and (111) heterojunctions. Dashed lines represent atomic planes parallel to the interface plane.

being defined in Fig. 3. In the same figure we have plotted the potential shape (i.e., the  $U_{in}$  and  $\Delta E_v$ ), while the calculated band offsets are given in Table I, where they are compared to the results of other calculations.

We have first to explain the difference between our results (first column) and those of Ref. 12 (second column) which are, in principle, equivalent calculations. In case of polar interfaces, there is a slight discrepancy between both results. There may be two reasons for this: (i) a very slight difference can be due to the use of different bulk parameters (those given in Appendix A differ slightly from Vogl parameters<sup>14</sup>) but we have checked that this effect is very weak; (ii) an improved accuracy on the charges due to an increased number of special points in the Brillouin zone, and a different integration contour in the complex energy plane (we have checked that in all cases our accu-

TABLE I. GaAs/AlAs band offsets (in eV).

Orientation	This work	Flores (Ref. 12) charge neutrality condition	Flores (Ref. 12) self-consistent calculation	Martin (Ref. 10) self-consistent local density calculation
(100)	0.49	0.44	0.37	0.37
(110)	0.63	0.36	0.32	0.37
(111)	0.51	0.40	0.37	0.39
$(\bar{1}\bar{1}\bar{1})$	0.47	0.40	0.35	

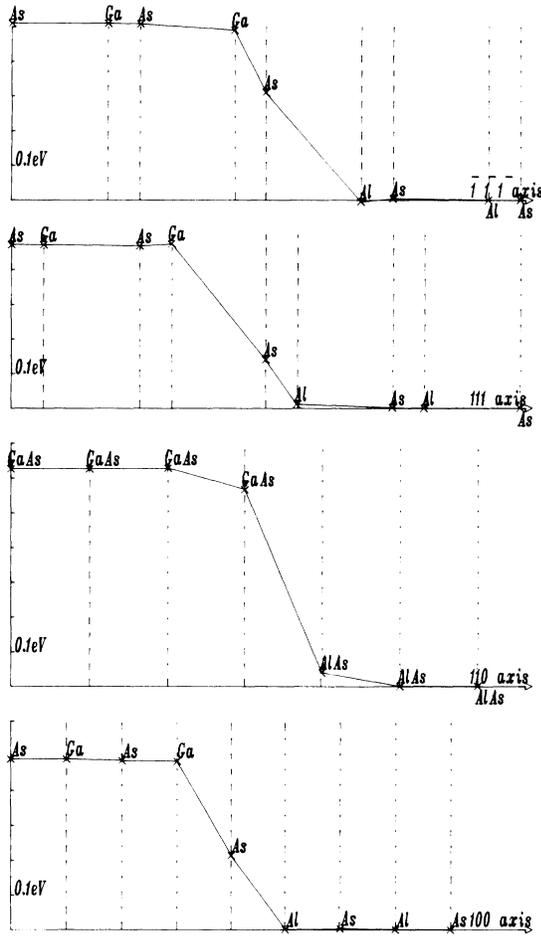


FIG. 3. Potential shapes at different GaAs/AlAs heterojunctions. Dashed lines represent atomic planes parallel to the interface plane.

racy on the charges was better than  $10^{-3}$  electron).

On the other hand, for the (110) interface the great discrepancy between both calculations is simply due to the fact that they correspond to different tight-binding descriptions of interface interactions.  $\Delta E_v = 0.63$  eV has been obtained as described in Sec. II: As there is a common anion, interface interactions are approximated by bulk interactions [Eq. (1)], whereas  $\Delta E_v = 0.36$  eV corresponds to the use of average bulk interactions through the interface. Such a discrepancy could appear a bit surprising, as bulk interactions are not very different in GaAs and AlAs. In order to explain this fact we have calculated  $\Delta E_v$  using Eq. (2) and obtained  $\Delta E_v = 0.27$  eV (the difference between our 0.27 value and the 0.36 value of Ref. 14 can be explained in the same way as for polar interfaces).

The mechanism of the difference between the use of Eq. (1) and of Eq. (2) can be simply explained using a bond orbital model as suggested in Fig. 4: As the two interface planes are connected by  $(\beta_1, \beta_2)$  there are some charge transfers from cations to anions across the interface plane

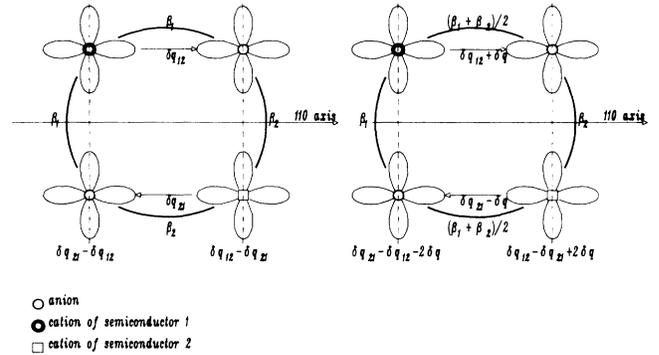


FIG. 4. Atomic charge transfers near interface for different descriptions of interface interactions: left-hand scheme corresponds to Eq. (1) description and right-hand scheme to Eq. (2) description (see text). Arrows indicate charge transfer across interface plane. On the lower line are indicated charge transfers by plane parallel to the interface plane (represented by dashed lines).

( $\delta q_{12}$  from Ga to As atoms and  $\delta q_{21}$  from Al to As atoms). These charge transfers lead to a dipole  $[\pm(\delta q_{21} - \delta q_{12})]$  which is essential to the determination of  $\Delta E_v$ . If now the interactions  $(\beta_1, \beta_2)$  are replaced by the mean values, i.e.,

$$\left[ \beta_1 + \frac{\beta_2 - \beta_1}{2}, \beta_2 - \frac{\beta_2 - \beta_1}{2} \right],$$

to first order  $\delta q_{12}$  will be changed to  $\delta q_{12} + \delta q$ , whereas  $\delta q_{21}$  will be modified to  $\delta q_{21} - \delta q$ . This leads to a cumulative effect: Both modifications in charge transfers modify in the same way the dipole which becomes  $\pm(\delta q_{21} - \delta q_{12} - 2\delta q)$ . From this change of dipole will result a change in  $\Delta E_v$ . We have calculated charges near an interface modeled by using Eqs. (1) and (2). The mechanism just described has been observed. For AlAs and GaAs,  $(\beta_1 - \beta_2)/2$  is of the order of 0.1 eV. Then we find  $2\delta q$  equal to 0.08 electron. As  $\Delta Q/\Delta E_v \simeq 0.2$ , one obtains the difference [0.26 eV for Eq. (2), 0.63 eV for Eq. (4)] between the two offsets. As explained in Sec. II, with the use of two-center interactions, the natural description is Eq. (1), as an interfacial cation atom has the same environment as in bulk.

We have estimated the accuracy of our calculations to be 0.01 eV. If we consider only the polar interface we obtain (Table I) a slight dependence of the band offsets on the face orientation:  $\Delta E_v = 0.49 \pm 0.02$  eV. We can observe a good agreement between our (100) values (0.49 eV) and recent experimental data<sup>2,6</sup> (0.45–0.56 eV). One experimental work<sup>5</sup> has studied the orientation dependence of band offsets. In this work only (100) and (311) orientations were considered. But there is no experimental observation that invalidates the theoretical difference found here between the (110) and usual polar interfaces: we have obtained, indeed, that for (110) nonpolar interface the band offset (0.63 eV) is quite different from those for polar heterojunctions ( $0.49 \pm 0.02$  eV).

In Fig. 3 are reported potential shapes near the hetero-

TABLE II. CdTe/HgTe band offsets (in eV).

Orientation	This work	Flores (Ref. 12) charge neutrality condition	Flores (Ref. 12) self-consistent calculation
(100)	0.38	0.54	0.53
(110)	0.31	0.30	0.28
(111)	0.38	0.43	0.40
( $\bar{1}\bar{1}\bar{1}$ )	0.38	0.43	0.41

junction. We can observe that the potential barrier spreads over three atomic planes (about 4 Å). This should be taken into account in calculations on ultrathin superlattices (where layer widths are a few tens of angstroms).

### B. CdTe/HgTe systems

CdTe/HgTe band offsets can be calculated using the same approach. Bulk description of CdTe and HgTe are those given in Ref. 20. We have checked that considering spin-orbit coupling (SOC) does not strongly modify the calculated band offsets [for (111) orientation  $\Delta E_v = 0.39$  eV if SOC is considered, and  $\Delta E_v = 0.38$  eV if not]. These calculated band offsets (where SOC is not taken into account) are given in Table II, where they are compared to the results of other calculations. We obtain once more that the band offset for the (110) interface (0.31 eV) is different from those for polar heterojunctions (0.38 eV). The value for (111) face is in good agreement with recent experimental evidence ( $0.35 \pm 0.06$  eV).<sup>21</sup> Differences with results<sup>11,12</sup> can be explained in the same way as for GaAs/AlAs systems. A more detailed study of CdTe/HgTe heterojunction and of the band offset differences between polar and nonpolar interfaces will be the object of a forthcoming publication.

## IV. CONCLUSION AND EXTENSIONS

In this work we have described a tight-binding calculation of band offsets. We have obtained—for polar interfaces—a slight dependence of band offsets on the face orientation. On the other hand, we obtain a clear difference between (110) and usual polar interfaces. We have also pointed out that this type of calculation is very sensitive to charge precision. Thus charge modifications have to be calculated very cautiously. Here we have used a “local-charge-neutrality condition” and an interesting development of this work could be to consider the effect of complete self-consistency on the band offsets. The calculation described here can be directly applied to any heterojunction with a common anion or where interface bonds correspond to an existing bulk material. For other heterojunctions a serious problem of parametrization appears, as there is no longer a “natural” description of interface interactions. This problem was previously ignored. It would be interesting to solve it in order to validate or invalidate existing tight-binding band offset calculations in such cases.

## ACKNOWLEDGMENTS

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### APPENDIX A: TIGHT-BINDING PARAMETERS OF GaAs AND AlAs IN AN $sp^3s^*$ MODEL

Tight-binding parameters of GaAs and AlAs in an  $sp^3s^*$  model are reported in Table III. For GaAs, they correspond to those given in Ref. 14, and for AlAs they have been slightly modified to obtain direct and indirect bandgap width given in Ref. 19, i.e.,  $E(\Gamma-X) = 2.16$  eV,  $E(\Gamma-L) = 2.36$  eV, and direct gap equal to 2.95 eV. In this approximation only nearest-neighbor interactions are taken into account in a two center approximation.

### APPENDIX B: CALCULATION OF THE CHARGES $q_{in}$

We have shown that a precision of 0.01 eV in  $\Delta E_v$  requires us to know  $q_{in}$  with an accuracy of the order of 0.001e. To reach this precision we use the following numerical procedure: (a) Charges are obtained by integration of Green’s functions up to  $E_F$ . (b) Green’s functions

TABLE III. Tight binding parameters (in eV) of GaAs and AlAs, in an  $sp^3s^*$  model. The notations are those of Ref. 14.

Tight-binding parameters	GaAs	AlAs
$E(sa)$	-8.3431	-7.9473
$E(pa)$	1.0414	0.8933
$E(s^*a)$	7.5412	7.3930
$E(sc)$	-2.6569	-1.5827
$E(pc)$	3.6685	3.4967
$E(s^*c)$	6.7397	6.6373
$V(s,s)$	-6.4513	-7.0281
$V(x,x)$	1.9546	1.7673
$V(x,y)$	5.0779	3.6922
$V(sa,pc)$	4.4800	4.4272
$V(sc,pa)$	5.7839	4.5084
$V(s^*a,pc)$	4.4378	4.1392
$V(pa,s^*c)$	4.8083	3.3886

are calculated by the decimation technique,<sup>22</sup> at special points of the Brillouin zone.<sup>23</sup> A summation over these special points will give the total Green's functions. Let us notice that the interface breaks one of the symmetries of the bulk system so that one can no longer work with the usual reduced first Brillouin zone in the case of polar interfaces. In the (100) case,  $\frac{1}{4}$  instead of  $\frac{1}{8}$  of the first Brillouin zone and in the (111) [or  $(\bar{1}\bar{1}\bar{1})$ ] case,  $\frac{1}{6}$  instead of  $\frac{1}{2}$  of the first Brillouin zone has to be considered.

In the decimation technique, poles on the real axis prevent us from calculating the Green's function for real energies. The calculation can be only done in the complex plane. The integrated density of states is then obtained by integration along a contour surrounding the poles. The method is quite similar to the one used for bulk defect.<sup>24</sup> At fixed real energy  $E_F$  at midgap, we integrate from  $E_F - i\varepsilon_n$  to  $E_F + i\varepsilon_n$  ( $\varepsilon_n = 1$  eV) with a SPLINE interpolation done with 20 calculated points. From  $E_F + i\varepsilon_n$  to  $E_F + i\infty$ , we use 16-G Legendre points. The integration over half a circle to close the contour is done analytically at infinite radius.

#### APPENDIX C: VALIDITY OF THE ZERO CHARGE APPROXIMATION

Near a heterojunction, one can write (Fig. 5)

$$E_{v1} + \Delta E_v = E_{v2} + V_{\text{dip}}, \quad (\text{C1})$$

where  $E_{v1}$  and  $E_{v2}$  are the top of the valence bands referred to the zero electrostatic potential in the bulk infinite semiconductors,  $\Delta E_v$  the valence-band offset, and  $V_{\text{dip}}$  the heterojunction dipole layer. Due to surface dipole layers  $E_{v1}$  and  $E_{v2}$  are not equal to semiconductor work functions. Then we get

$$\Delta E_v = V_{\text{dip}} + \Delta E_v^0 \quad \text{with} \quad \Delta E_v^0 = E_{v2} - E_{v1}. \quad (\text{C2})$$

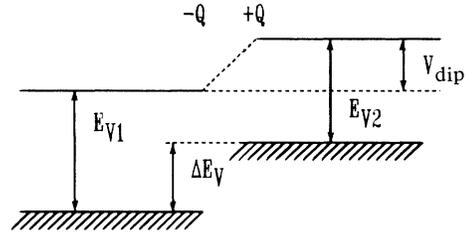


FIG. 5. Different energy levels near an heterojunction (all quantities are defined in Appendix C).

For zero charge transfer, one gets

$$\Delta E_v^{\text{ZC}} = V_{\text{dip}}^{\text{ZC}} + \Delta E_v^0, \quad (\text{C3})$$

where  $V_{\text{dip}}^{\text{ZC}}$  is the value obtained with the local neutrality condition. If the self-consistent result is close to the zero-charge result one can linearize the charge transfer  $Q$  across the heterojunction

$$Q = -\chi(V_{\text{dip}} - V_{\text{dip}}^{\text{ZC}}). \quad (\text{C4})$$

If we write

$$Q = CV_{\text{dip}}, \quad (\text{C5})$$

where  $C$  is the capacitance of the dipole layer, we get

$$\Delta E_v = \Delta E_v^{\text{ZC}} \frac{\chi/C}{1 + \chi/C} + \Delta E_v^0 \frac{1}{1 + \chi/C}. \quad (\text{C6})$$

The limit  $\chi/C$  equal zero corresponds to neglect the heterojunction dipole layer ( $V_{\text{dip}} = 0$ ) whereas  $\chi/C \gg 1$  gives the zero charge transfer condition. If the charge transfer only occurs between two planes near the heterojunction,  $\chi$  is close to 0.2 electron/eV and  $\chi/C \simeq 6$ . This shows the importance of an accurate evaluation of  $\Delta E_v^0$ .

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