

Theoretical study of band offsets at semiconductor interfaces

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We present a first-principles approach to deriving the relative energies of valence and conduction bands at semiconductor interfaces, along with a model which permits a simple interpretation of these band offsets. Self-consistent density-functional calculations, using *ab initio* nonlocal pseudopotentials, allow us to derive the minimum-energy structure and band offsets for specific interfaces. Here we report results for a large number of lattice-matched interfaces, which are in reasonable agreement with reported experimental values. In addition, our systematic analysis leads to the important conclusions that, for the cases considered, the offsets are independent of interface orientation and obey the transitivity rule, to within the accuracy of our calculations. These are necessary conditions for the offsets to be expressible as differences between quantities which are intrinsic to each of the materials. Based on the information obtained from the full interface calculations, we have developed a new and simple approach to derive such intrinsic band offsets. We define a reference energy for each material as the average (pseudo)potential in a "model solid," in which the charge density is constructed as a superposition of neutral (pseudo)atomic densities. This reference depends on the density of each type of atom and the detailed form of the atomic charge density, which must be chosen consistently for the different materials. The bulk band structures of the two semiconductors are then aligned according to these average potential positions. For many cases, these model lineups yield results close to those obtained from full self-consistent interface calculations. We discuss the comparison with experiments and with other model theories.

I. INTRODUCTION

It has become technologically possible to grow high-quality epitaxial interfaces between two different semiconductors, using techniques such as molecular-beam epitaxy. The most important parameters characterizing such heterojunctions are the valence- and conduction-band discontinuities. These discontinuities can form a barrier for carrier transport across the interface; the knowledge of these quantities is therefore essential for calculating the transport properties of the interface, or the electrostatic potential in a heterojunction device. Examples of such novel semiconductor structures include quantum-well lasers, high-speed modulation-doped field-effect transistors, and superlattice photodetectors. Measured experimental values for band lineups are not well established yet, even though considerable progress has been made in growth and analysis techniques. In this paper, we will present a theoretical approach to deriving the band offsets.

Let us suppose we know the band structures of the semiconductor bulk materials A and B . We now want to figure out what the band structure looks like around an interface A/B . It is only in a very narrow region around the junction that the potential will be changed from its shape in the respective bulk materials, as we will show. Band bending caused by space-charge layers occurs on a length scale that is much larger than the atomic distances

over which the band offsets occur; therefore, the bands can be considered to be flat on this scale, except for the sharp discontinuity at the interface. We are then confronted with the problem of how to line up these bulk bands with respect to one another, which amounts to determining the lineup of electrostatic potentials. This type of information cannot be obtained from regular bulk calculations alone. For an infinite solid, no absolute energy reference is provided by the calculations (i.e., no "vacuum zero" is present to which other energies could be referred).¹ Therefore one cannot compare separate calculations on different solids. The fundamental reason for this is the long range of the Coulomb interaction: the charge distribution at a surface or an interface will determine the position of the energy levels deep in the bulk.

A number of model theories²⁻⁶ have been developed which attempt to predict the lineups from information on the bulk alone; they necessarily rely on certain assumptions to establish an absolute energy scale, to which values for different materials can be referred. The electron affinity rule² assumed that the energy difference between the conduction band and the vacuum level, as measured at a surface, would be fixed, and derived conduction-band discontinuities in this fashion. Frenley and Kroemer³ attempted to identify a reference level in each semiconductor that would correspond to the vacuum level. Harrison's theory of natural band lineups⁴ established an absolute energy scale by referring everything to energy

eigenvalues of the free atom. A very different approach has been developed by Tejedor and Flores,⁵ and more recently, by Tersoff.⁶ Their model is based upon simple screening arguments to define a “neutrality level” for each semiconductor, which will be aligned when an interface is formed.

All of these model theories rely on information about the bulk alone, and do not provide a complete description of the electron distribution at the interface. The only way to obtain a full picture of this effect is to perform a calculation in which the electrons are allowed to adjust to the specific environment created by the interface. This can be accomplished by performing self-consistent calculations, which will correctly describe the electrostatic potential shift that determines the lineups. Density-functional theory provides a fundamental theoretical framework to address this problem, and has the advantage that one can use the same methods which have been applied to a wide variety of solid-state problems.⁷ Pickett *et al.*⁸ and Kunc and Martin⁹ have performed calculations which followed this approach; however, they used empirical pseudopotentials instead of the more recent *ab initio* pseudopotentials, and they only studied a small number of interfaces.

In this paper, we will carry out a systematic study of the band offset problem for a large number of heterojunctions; preliminary results for some of these systems have been reported elsewhere.¹⁰ Our calculations are performed on a superlattice geometry, and based on local-density-functional theory,¹¹ applied in the momentum space formalism,^{12,13} and using nonlocal norm-conserving pseudopotentials.¹⁴ From the self-consistent potentials we obtain information about potential shifts at the interface. Combining this with bulk band-structure calculations will allow us to derive values for valence- and conduction-band discontinuities. Spin-orbit splitting effects in the valence bands are added in *a posteriori*. We also need to address the “band-gap problem,”^{15–17} and examine to what extent the local-density approximation (LDA) is able to produce a reliable description of these heterojunction systems. Our discussion will indicate that for the semiconductors studied here the lineup of the bands should not be greatly modified by the known corrections to the local-density approximation.

Self-consistent calculations such as those performed in the present study provide a way to take all the effects of the electronic structure of the interface into account. This also implies that the results do not immediately tell us what physical mechanisms are dominant in determining the lineups. It is therefore important to systematically analyze a large number of interfaces, which will allow us to extract some general features of the lineup mechanism. In particular, we study the dependence of the lineups on interface orientation, and also examine to what extent the lineup mechanism can be considered to be linear. Linearity can be tested by checking whether transitivity is obeyed; it implies that the lineups can be obtained as a difference between quantities which are *intrinsic* to each semiconductor.

Based upon the information obtained from the full self-consistent calculations, we have developed a simple model to derive the lineups. We divide the problem into

one part which can be expressed as the difference between quantities which are *intrinsic* to each of the materials, and another which involves corrections due to the detailed electronic charge density at the interface. To define appropriate intrinsic quantities, we choose to describe the bulk solids by a superposition of neutral atoms. The average potential in such a “model solid” can be found on an absolute scale from atomic calculations, and is not influenced by boundary effects. At the junction between two model solids, a shift in the average potentials occurs, which we take as the reference with respect to which any additional dipole corrections will be measured. The bulk band structures of the two materials are then aligned according to these average potential positions. A short description of this model was given elsewhere.¹⁸ For non-polar interfaces, the model lineups yield results close to those obtained from full self-consistent interface calculations, and to reported experimental values. This indicates that for these interfaces the additional dipole contributions are small. Furthermore, these lineups are independent of interface orientation and obey the transitivity rule, corresponding to what was found from the *ab initio* calculations.

We have applied our methods to both lattice-matched and strained-layer interfaces between pairs of group-IV elements and III-IV and II-VI compound semiconductors. Interfaces between materials which are lattice mismatched are receiving considerable attention nowadays; the strains which are present in such strained-layer structures have important effects on the electronic structure.¹⁹ We have performed extensive calculations for such systems, in particular for the Si/Ge interface, the results of which have been reported elsewhere.^{18,20,21} In this paper we will concentrate upon lattice-matched systems. In the next section, we will describe the self-consistent calculations, and illustrate them with the example of a GaAs/AlAs interface. In Sec. III, we will give an overview of the broad range of lattice-matched systems that we studied, and derive some important and general conclusions. Section IV contains a description of the model solid approach that allows us to determine the lineups in a simpler way. We present a comparison with other theories and with experiment in Sec. V. Section VI concludes the paper.

II. SELF-CONSISTENT CALCULATIONS

A. Derivation of band lineups

In this paper, we will be reporting results for lattice-matched interfaces. We consider two semiconductors to be matched if the difference in lattice constant is less than 0.5%. We then fix the materials to have the same lattice constant in the interface calculation; the values we have used are listed in Table I. The geometry we use for the interfaces in this study is an ideal structure, in which the zinc-blende (or diamond) structure is continued throughout the system, with an abrupt change in the type of material right at the junction, and no displacements of the atoms from their ideal positions. We have performed density-functional total energy calculations for representative cases (GaAs/AlAs, and closely related checks²¹ on

TABLE I. Lattice constant a , spin-orbit splitting (Ref. 25) and configuration (Ref. 35) used in atomic calculations for selected semiconductors.

Semiconductor	a (Å)	Spin-orbit splitting (eV)	Configuration
Si	5.43	0.04	$s^{1.46}p^{2.54}$
Ge	5.65	0.30	$s^{1.44}p^{2.56}$
AlAs	5.65	0.28	Al, $s^{1.11}p^{1.89}$; As, $s^{1.75}p^{3.25}$
AlP	5.43	0.04	Al, $s^{1.11}p^{1.89}$; P, $s^{1.75}p^{3.25}$
AlSb	6.08	0.65	Al, $s^{1.11}p^{1.89}$; Sb, $s^{1.75}p^{3.25}$
GaAs	5.65	0.34	Ga, $s^{1.23}p^{1.77}$; As, $s^{1.75}p^{3.25}$
GaP	5.43	0.08	Ga, $s^{1.23}p^{1.77}$; P, $s^{1.75}p^{3.25}$
GaSb	6.08	0.82	Ga, $s^{1.23}p^{1.77}$; Sb, $s^{1.75}p^{3.25}$
InAs	6.08	0.38	In, $s^{1.38}p^{1.62}$; As, $s^{1.75}p^{3.25}$
ZnSe	5.65	0.43	Zn, $s^{1.02}p^{0.98}$; Se, $s^{1.86}p^{4.14}$

Si/Ge) to examine the validity of this assumption. We found that the ideal structure is very close to the minimum-energy configuration, with very small forces acting on the atoms. More importantly, we studied what effect the small displacements that might occur (on the order of 0.05 Å) would have on the band offsets. For nonpolar interfaces as studied here we found the effects to be negligible. However, we should note that displacements of charged atoms at polar interfaces would be expected to produce dipole shifts, as was indeed found in the studies in Ref. 9.

A major problem that has to be faced in calculating the electronic structure of an interface is the loss of translational symmetry, which is essential for using a reciprocal

space formulation of the problem. The actual calculations are therefore performed on a superlattice, consisting of slabs of the respective semiconductors in a particular orientation. A typical (110) interface between two semiconductors, GaAs and AlAs, is sketched in Fig. 1(a). We also indicate a supercell appropriate for calculating the properties of this interface; it contains 12 atoms and 2 identical interfaces. Of course, what we emphasize here are the results for an isolated interface. These can be derived from our calculations to the extent that the interfaces in the periodic structure are well separated. We will establish *a posteriori* that this is the case, by examining charge densities and potentials in the intermediate regions, and showing them to be bulklike.

The self-consistent calculations are performed within the framework of local-density-functional theory,¹¹ applied in the momentum space formalism.^{12,13} We use nonlocal, norm-conserving, *ab initio* pseudopotentials;¹⁴ this term indicates that these potentials are generated using only theoretical calculations on atoms, without introducing any type of fitting to experimental band structures or other properties. All elements are therefore treated in the same way, which is particularly important when we want to include different materials in the same calculation, as for an interface. This is not true for the empirical pseudopotentials which have been used in previous interface calculations.^{8,9} For Zn, the pseudopotential includes the 3*d* electrons as part of the core. We obtain self-consistent solutions for the charge density and the total potential, which is the sum of ionic, Hartree, and exchange-correlation potentials. The latter is calculated using the Ceperley-Alder form.²² The first cycle requires a trial potential, a possible choice for which is the ionic potential screened by the dielectric function of a free-electron gas. An even better choice in many instances is the potential corresponding to a superposition of free-atom charge densities. Convergence of the self-consistent iterations is obtained with the help of the Broyden scheme.²³

We include plane waves with kinetic energy up to 6 Ry in the expansion of the wave functions (corresponding to more than 650 plane waves in some cases). A set of 4 special points was used for sampling k space.²⁴ We will show later that these choices are sufficient for deriving the quantities we are interested in here. In the final self-consistent solution, a redistribution of electrons occurs in

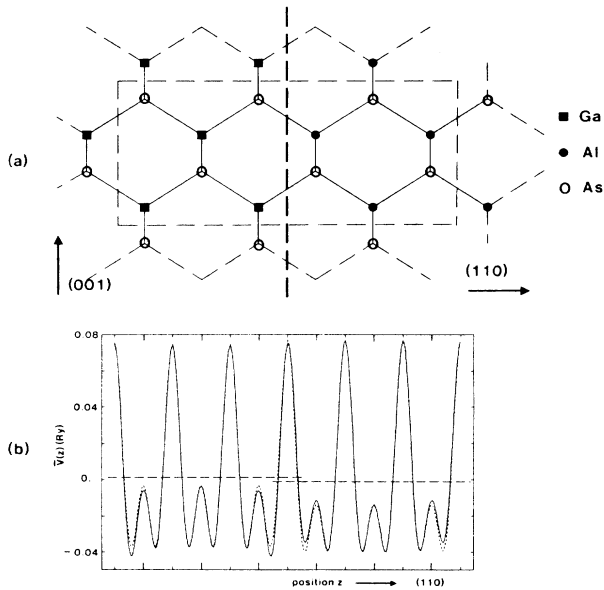


FIG. 1. (a) Schematic representation of a GaAs/AlAs (110) interface. The supercell used in the interface calculations is indicated in dotted lines; it contains 12 atoms and 2 identical interfaces. (b) Variation of the $l=1$ component of the total potential $\bar{V}(z)$ [as defined in Eq. (1)] across the (110) interface. The dashed lines represent the corresponding potentials for the bulk materials. These coincide with $\bar{V}(z)$ in the regions far from the interfaces. However, the average levels of the two bulk potentials (dashed horizontal lines) are shifted with respect to one another.

the interface region. The resulting self-consistent potential across the supercell is plotted in Fig. 1(b), for the example of GaAs/AlAs. Because the *ab initio* pseudopotentials are nonlocal, the total potential consists of different parts corresponding to different angular momenta l . We only show the $l=1$ part of the potential here; this is the most important one in determining the lineup of the p -like valence bands. In the plot, the variation of the space coordinate r is limited to the component perpendicular to the interface, and values of the potentials are averaged over the remaining two coordinates, i.e., in the plane parallel to the interface:

$$\bar{V}(z) = [1/(Na^2)] \int \int V(\mathbf{r}) dx dy. \quad (1)$$

In the regions far from the interface, the crystal should recover properties of the bulk. Therefore we also plot (broken lines) the potentials determined separately from calculations on bulk GaAs and AlAs. One sees that already one layer away from the interface the potential assumes the form of the bulk potential. Similar results hold for the charge density. This confirms, *a posteriori*, that the two interfaces in our supercell are sufficiently far apart to be decoupled, at least as far as charge densities and potentials are concerned. The average levels of the potentials which correspond to the bulk regions are also indicated in Fig. 1(b). We denote these average levels by \bar{V}_{GaAs} and \bar{V}_{AlAs} , and define the shift $\Delta\bar{V} = \bar{V}_{\text{GaAs}} - \bar{V}_{\text{AlAs}}$.

To get information about band discontinuities, we still have to perform the band calculations for the bulk materials. These were carried out with a 12-Ry cutoff; tests have shown that the choice of this cutoff is not critical for deriving the valence-band lineups. We find that the valence-band maximum in GaAs is 9.60 eV above the average potential \bar{V}_{GaAs} . In AlAs, the valence band occurs at 9.29 eV above \bar{V}_{AlAs} . From Fig. 1(b), we find $\Delta\bar{V} = 0.035$ eV. Figure 2 illustrates the resulting band lineups; we find a discontinuity in the valence band of $\Delta E_v = 0.34$ eV (upward step in going from AlAs to GaAs). We did not include spin-orbit splitting in our density-functional calculations. These effects can be added in *a posteriori*, by using experimental values for spin-orbit splittings.²⁵ For GaAs/AlAs, this brings the discontinuity to a value of $\Delta E_v = 0.37$ eV.

B. Accuracy

We estimate the inaccuracy of our calculations to be on the order of 0.05–0.10 eV. We have checked the convergence with respect to energy cutoff by increasing the cutoff to 9 Ry; this caused a change in $\Delta\bar{V}$ of less than 0.03 eV, in the direction of shifting ΔE_v towards higher values. We have also performed test calculations, using a local potential, to determine whether the interfaces in our supercell are sufficiently well separated. Increasing the number of atoms in the supercell to 16 resulted in a negligible change (less than 0.02 eV) in $\Delta\bar{V}$, thus confirming that a cell with 12 atoms suffices for our purposes. We also checked how good an assumption it is to put the atoms in the ideal structure. We calculated the forces on the atoms, for a GaAs/AlAs(110) interface, with 12

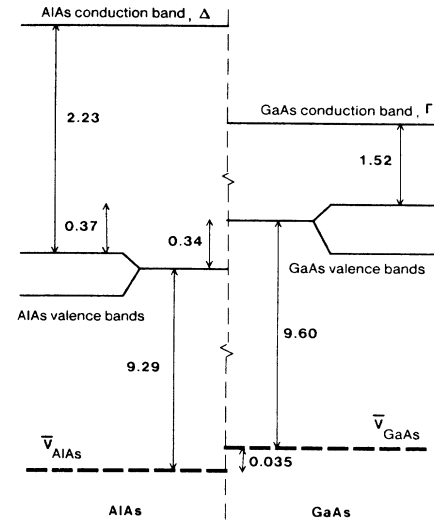


FIG. 2. Derivation of band lineups: relative position of the average potentials \bar{V}_{AlAs} and \bar{V}_{GaAs} , and of the AlAs and GaAs valence and conduction bands. All values shown are derived with the $l=1$ angular momentum component chosen as the reference potential; the band lineups, however, are unique and independent of this choice. Valence-band splittings due to spin-orbit splitting are indicated separately. Experimental band gaps were used to derive conduction-band positions.

atoms in the unit cell; they turned out to be smaller than 0.03 mdyne. This would lead to changes in the atomic positions smaller than 0.03 Å. We have checked that displacements of this size have a negligible effect on the band lineups. All this confirms that our choice of parameters allows us to obtain a numerical accuracy in deriving the lineups of 0.05–0.10 eV. Similar results were found for the Si/Ge interface.²¹

It is also appropriate to consider what effects the use of the local-density approximation (LDA) has upon the accuracy of our results. It is well known that the LDA severely underestimates the magnitudes of band gaps in semiconductors. More generally, the positions of the bulk bands with respect to the reference potential \bar{V} can be subject to significant corrections, which can only be obtained by going beyond the LDA. This has been the subject of extensive recent theoretical investigations.^{15–17} Precise information about the required corrections to the LDA for all semiconductors is not yet available at this time. Such corrections would need to be taken into account in the derivation of ΔE_v and ΔE_c . We expect, though, that for many of the systems that we studied the value of ΔE_v will not be significantly affected. From our comparison of LDA eigenvalues with experimental band structures, and from theoretical analysis,¹⁷ there is evidence that the corrections needed to bring the conduction bands into agreement with experiment are fairly uniform for all conduction-band points (except for the Γ point, which, however, bears little relation to the conduction band as a whole, and has little weight in the Brillouin zone). As long as these corrections to the LDA are similar for the two materials on either side of the interface, the *relative* positions of valence and *representative* conduction bands

are still given reliably by our lineup scheme. This seems to be true for most of the materials in Table I. The discrepancies tend to be larger between narrow-gap and wide-gap semiconductors (such as Ge and ZnSe), in which case somewhat larger errors (up to 0.3 eV) may occur.

In addition, the change in reference potential $\Delta\bar{V}$ contains long-range electrostatic dipole terms. Since these are given strictly in terms of the ground-state charge density, they would be correctly given by the exact density functional. However, the LDA may introduce errors, which one would expect to affect the interface dipole if the errors are different on the two sides of the interface. We have argued²¹ that our results for $\Delta\bar{V}$ for Si/Ge are not greatly affected because the LDA errors are similar in the materials. Thus, just as in the previous paragraph, we conclude that corrections to the dipole terms should be small for interfaces between similar materials, such as most of the cases studied here, but may be larger effects for interfaces between more dissimilar materials.

In terms of deriving values for ΔE_c , we are confronted with the problem that many of the materials we are studying are direct gap semiconductors. The conduction band at Γ is not representative for the conduction-band structure as a whole, and may show large discrepancies; it is also quite sensitive to the energy cutoff, and to the inclusion of relativistic effects.²⁶ Because of these uncertainties in the gap at Γ , we will use experimental information about band gaps²⁵ to include conduction bands into the picture. We thus report our *ab initio* results for valence-band offsets, and find the conduction-band lineup by subtracting the valence-band discontinuity from the ex-

perimental band-gap difference. For the GaAs/AlAs interface this leads to $\Delta E_c = 0.34$ eV (higher in AlAs, with the lowest conduction band in AlAs situated at Δ).

III. RESULTS FROM SELF-CONSISTENT CALCULATIONS

A. Overview of results for lattice-matched interfaces

We have studied a variety of lattice-matched (110) interfaces, the results for which are given in Table II. In all cases, the convention is used that a positive value for the discontinuity at a junction A/B corresponds to an upward step in going from A to B . For interfaces between a group-IV element and a III-V compound, the (110) orientation is the only one which avoids charge accumulation without the need for mixing at the interface.²⁷ Our values have been adjusted to include spin-orbit splitting, the experimental values for which are listed in Table I. The correction to ΔE_v due to spin-orbit splitting is typically smaller than 0.05 eV. The only case in which it is really sizable is InAs/GaSb, where it increases ΔE_v by 0.15 eV. For GaSb and AlSb, there is some uncertainty in the value of the spin-orbit splitting. The result $\Delta E_v = 0.38$ eV in Table II was derived using the spin-orbit values from Table I. If the spin-orbit splittings in these two materials were equal, the value of ΔE_v would be 0.32 eV.

The column “empirical pseudopotentials” in Table II contains values derived by performing self-consistent density-functional calculations very similar to ours, but with empirical pseudopotentials.⁸ We notice a significant

TABLE II. Heterojunction band lineups for lattice-matched (110) interfaces, obtained by self-consistent interface calculations (SCIC), and by the model solid approach. Other theoretical and experimental results are listed for comparison.

Heterojunction	SCIC	Model solid	ΔE_v (eV)				LMTO ^c	Tersoff theory ^d	Experiment
			Empirical pseudopotential ^a	Harrison ^b					
				“Natural”	“Pinned”				
AlAs/Ge	1.05	1.19		0.70	0.78	0.73	0.87	0.95 ^e	
GaAs/Ge	0.63	0.59	0.35	0.67	0.66	0.24	0.32	0.56 ^f	
AlAs/GaAs	0.37	0.60	0.25	0.03	0.12	0.49	0.55	0.55 ^g	
AlP/Si	1.03	1.16		0.87	0.79	0.93	0.91		
GaP/Si	0.61	0.45		0.86	0.69	0.75	0.45	0.80 ^h	
AlP/GaP	0.36	0.70		0.01	0.10	0.18	0.46		
ZnSe/GaAs	1.59	1.48	2.0±0.3	1.42	1.35	1.75	1.20	1.10 ⁱ	
ZnSe/Ge	2.17	2.07	2.0±0.3	2.09	2.01	1.99	1.52	1.52 ^j	
InAs/GaSb	0.38	0.58		0.72	0.42	0.36	0.43	0.51 ^j	
AlSb/GaSb	0.38	0.49		0.09	0.18	0.17	0.38	0.45 ^k	

^aReference 8.

^bReference 48.

^cReference 49.

^dJ. Tersoff, J. Vac. Sci. Technol. B 4, 1066 (1986).

^eM. K. Kelly, D. W. Niles, E. Colavita, G. Margaritondo, and M. Henzler (unpublished); quoted in G. Margaritondo, Phys. Rev. B 31, 2526 (1985).

^fJ. R. Waldrop, E. A. Kraut, S. P. Kowalczyk, and R. W. Grant, Surf. Sci. 132, 513 (1983).

^gReference 39.

^hP. Perfetti, F. Patella, F. Sette, C. Quaresima, C. Capasso, A. Savoia, and G. Margaritondo, Phys. Rev. B 30, 4533 (1984).

ⁱS. P. Kowalczyk, E. A. Kraut, J. R. Waldrop, and R. W. Grant, J. Vac. Sci. Technol. 21, 482 (1982).

^jReference 43.

^kJ. Menéndez and A. Pinczuk (private communication).

difference with our values, due to our use of *ab initio* pseudopotentials, compared to their empirical pseudopotentials (fitted to reproduce experimental band structures). If we use those same pseudopotentials in our calculations, we reproduce their result (within the numerical accuracy of 0.05 eV). This indicates that the essential difference is in the choice of the pseudopotential—the *ab initio* pseudopotential providing a better justified starting point. We will discuss the other entries in the table after we have presented the model solid approach.

B. Dependence on interface orientation

For the GaAs/AlAs system, we have also studied other interface orientations. In particular, for the (100) interface we find a valence-band discontinuity of 0.37 eV, the same as the value for the (110) interface. For (111), we find $\Delta E_v = 0.39$ eV. This indicates that ΔE_v does not depend on interface orientation, a result that was also found experimentally.²⁸ Let us note that this is not necessarily valid for pseudomorphic strained-layer systems, in which different strains associated with different interfaces can have sizable effects on the lineups, as discussed in Refs. 20 and 21. It also has been shown that rearrangements of atoms at polar interfaces can change the offsets.⁹ Within such limitations, we believe that the result that the offset is orientation independent can be considered an important general result for suitably chosen lattice-matched interfaces.

C. Pressure dependence of the lineups

We have also performed self-consistent interface calculations for GaAs/AlAs interfaces under hydrostatic pressure. Two groups²⁹ have performed photoluminescence experiments on GaAs/Ga_{1-x}Al_xAs heterojunctions, in order to vary the band offsets and to use this information to determine their magnitudes at zero pressure. In the interpretation of the experimental results, it was assumed that ΔE_v remains constant under pressure. It is appropriate to examine the validity of that assumption. Since the bulk moduli of the two materials are very similar (784 kbar for GaAs, and 733 kbar for AlAs), it is safe to assume that the only effect of hydrostatic pressure will be to decrease the lattice constant of the overall system, according to the relation:

$$P = -B \Delta V/V = -3B \Delta a/a,$$

where P is the pressure, B is the bulk modulus, V is the volume, and a is the lattice constant. We have therefore performed interface calculations at four different lattice constants, ranging from 5.65 to 5.50 Å, as well as the cor-

responding bulk calculations for the compressed solids. We found that

$$\begin{aligned} \Delta E_v &= \Delta E_v^0 - 0.64 \Delta V/V \\ &= \Delta E_v^0 + 0.82 \times 10^{-3} P, \end{aligned}$$

where ΔE_v^0 is the valence-band discontinuity at zero pressure, and P is expressed in kbar. This is to be compared, for instance, with the change in the GaAs direct band gap under pressure, which we calculate to be

$$\begin{aligned} \Delta E_g &= \Delta E_g^0 - 8.33 \Delta V/V \\ &= \Delta E_g^0 + 10.6 \times 10^{-3} P. \end{aligned}$$

We see that the change in ΔE_v is more than an order of magnitude smaller than the change in the gap; a pressure change of 10 kbar will increase the gap by 0.1 eV, but only change ΔE_v by less than 0.01 eV.

D. Transitivity

It is interesting to examine our results to establish the extent to which theory supports the proposition that the band offsets for any pair of semiconductors can be expressed as a difference of numbers *intrinsic* to each material. This has been observed from experiment,^{30,31} and is an implicit assumption in theories such as Refs. 2–6. It is clear that our full interface calculations do not assume linearity, i.e., we do *not* postulate that our heterojunction lineups be given by the difference of two numbers which would each be characteristic for a particular semiconductor, independent of which heterojunction it is used in. *A posteriori*, however, we can check how close our results are to linearity, by examining transitivity, i.e., whether the following equation is satisfied:

$$\Delta E_v(A,B) + \Delta E_v(B,C) = \Delta E_v(A,C) \quad (2)$$

where

$$\Delta E_v(A,B) = E_v(B) - E_v(A).$$

In Table III, we list values for these quantities, which allow us to conclude that the transitivity rule [Eq. (2)] is satisfied to better than 0.06 eV, which is on the order of the numerical accuracy of the calculations. It is interesting to note that transitivity also holds for strained-layer interfaces, taking the appropriate strains into account to construct pseudomorphic interfaces. We have checked this for Si/Ge/GaAs (results for Si/Ge and Si/GaAs were reported in Ref. 18) where Eq. (2) turned out to be satisfied to within 0.01 eV. The fact that transitivity is satisfied shows that the deviations from linearity are small. Together with the orientation independence, we believe that

TABLE III. Examination of transitivity [Eq. (2)] for various sets of systems. ΔE_v values are from Table II. The values in the last two columns are equal to within the numerical accuracy of the calculations, showing that transitivity is satisfied.

<i>A</i>	<i>B</i>	<i>C</i>	$\Delta E_v(A,B)$	$\Delta E_v(B,C)$	$\Delta E_v(A,B) + \Delta E_v(B,C)$	$\Delta E_v(A,C)$
AlAs	GaAs	Ge	0.37	0.63	1.00	1.05
AlP	GaP	Si	0.36	0.61	0.97	1.03
ZnSe	GaAs	Ge	1.59	0.63	2.22	2.17

this is indicative of the *intrinsic* nature of the band offsets for large classes of lattice-matched systems.

Our general conclusions regarding orientation independence and linearity indicate that in principle it is possible to derive the lineup by determining a reference level for each semiconductor, and lining up the band structures according to these reference levels. In the next section, we will describe how we define an appropriate level for each material.

IV. DEFINITION OF A REFERENCE MODEL SOLID

As we already pointed out, a pure bulk calculation cannot provide information about absolute energy positions. An absolute energy scale only enters into the problem if one does not deal with an infinite solid, but instead the crystal is terminated—i.e., by a surface. A particular choice of reference surface must be made, which will then allow us to express all energies with respect to the vacuum level. Our choice for terminating the solid should correspond as closely as possible to the situation at an interface; this immediately excludes using the structure of a real surface, which might involve complicated relaxation and reconstruction. Also, we do not want to perform a complete self-consistent calculation for a surface—since that would be computationally even harder than an interface calculation. We have therefore developed a model theory, which allows us to calculate the reference energy for a particular choice of reference surface. The model corresponds to a superposition of atomic charged densities, which is known to give reasonable results for a number of bulk properties. Mattheiss, for instance, used it to study energy bands of transition metals.³² Here it turns out to be particularly suited to the derivation of semiconductor interface properties. The model will be used *only* to find a value for the average electrostatic potential (on an absolute scale) for each semiconductor. The positions of the bands with respect to this average potential are still obtained from self-consistent calculations for the bulk crystals, as was described in the last paragraph of Sec. II A. Within this model we can thus line up the band structures for different crystals without the need for a self-consistent interface calculation of the type described in Sec. II A.

We construct the model solid by taking a superposition of neutral atomic spheres. The potential outside each such sphere goes exponentially to (an absolute) zero; this will be the zero of energy for the model solid. When we use such neutral, spherical objects to construct a semi-infinite solid, the presence of a surface will not induce any shift in the average potential, since no dipole layers can be set up. This feature of the model was also stressed in earlier work that used the overlapping spherical atomic charge-density approximation, for instance to calculate work functions.³³ This also means that the potential shift between two solids will only depend on “bulk” properties, and not on the specific arrangement of atoms at the interface.

One has to check, of course, that such a model solid can adequately represent the real crystal. This is not difficult to imagine in the case of elemental semiconductors, but

somewhat harder to understand for materials in which the bonds have more of an ionic character, such as the III-V or even the II-VI compounds. Apart from the *a posteriori* justification that the obtained results are quite good, we can also rely on information obtained from pseudopotential³⁴ or tight-binding³⁵ calculations on bulk materials. Examination of the distribution of electrons in the bonds shows that the number of electrons around each atom is approximately equal to its nuclear charge, i.e., one can still talk about “neutral spheres.”

Full information about the atomic potential can be obtained by performing an atomic calculation (of the Herman-Skillman type). Since all our calculations for the solid are based on pseudopotentials, we actually perform the atomic calculations on the “pseudoatom.” The choice of pseudopotential for this purpose is arbitrary, so long as the same ionic potential is used throughout the calculations. We now must find the average potential in the model solid, which is a superposition of atomic charge densities. The total potential is the sum of ionic, Hartree, and exchange and correlation potentials:

$$V^l = V^{\text{ion},l} + V^H + V^{\text{xc}}. \quad (3)$$

The superscript l on $V^{\text{ion},l}$ reflects the fact that we are working with nonlocal pseudopotentials.¹⁴ The choice of angular momentum component does not influence the final results, so long as we consistently use the same angular momentum component of the pseudopotential as our reference. The first two terms in (3) are linear in the charge density, and can therefore also be expressed as a superposition of atomic potentials. Their average value in the solid is

$$\bar{V}^{\text{ion},l} + \bar{V}^H = \sum_i (1/\Omega) \int (V_i^{\text{ion},l} + V_i^H) d\tau, \quad (4)$$

where Ω denotes the volume of the unit cell, and the index i runs over all atoms in the unit cell. Convergence is no problem in the numerical integration, since for each neutral atom the long-range part of the ionic potential (which is the same for each l) is canceled by the Hartree potential. The exchange and correlation potential V^{xc} is not linear in the charge density, and can therefore not be expressed as a superposition of atomic potentials. This contribution, however, is local in nature and does not depend upon the specific way in which we terminate the solid. It can easily be calculated for a bulk solid, and added in afterwards.

We illustrate the procedure with the example of an AlAs/GaAs interface. To perform the atomic calculations, we have to choose a configuration, i.e., the occupation x and y of the s and p orbitals: $s^x p^y$ (the d character of the bonds is small in the semiconductors that we studied here). Naturally, we want this choice to be as close as possible to the configuration that an atom would have in the solid. It is not easy to extract this type of information from pseudopotential calculations on the bulk crystal. Since angular momentum is not a good quantum number in the solid, there is no straightforward way to distinguish between s or p character of wave functions. We therefore extract these values from tight-binding calculations,³⁵ in which the choice of basis set provides a natural separation

between s and p states. We used $s^{1.23}p^{1.77}$ for Ga, $s^{1.11}p^{1.89}$ for Al, and $s^{1.75}p^{3.25}$ for As. The atomic charge density does not vary much when the configuration is changed; still, the average potentials tend to be rather sensitive to the choice of configuration. Although a change in configuration causes only small shifts in the long-range tail of the wave function, these changes at large r values may have a significant effect on the average. For Ga, going from an sp^2 to an s^2p configuration shifts the average potential up by 0.72 eV; the variation is close to linear. An analogous change for Al introduces a shift of 0.70 eV. This indicates that the uncertainties become less severe when we look at potential *differences*. For example, the lineup in the GaAs/AlAs system will be determined by the difference in average potential between Ga and Al; it is to be expected that the configurations will be similar for these atoms in GaAs and AlAs. Making the *same* change in the configuration on both sides will have no effect on the potential difference. We establish as our convention that atomic configurations will be used which are obtained from tight-bonding theory³⁵ for all systems that we study.

We then carry out the atomic calculations on the pseudoatom in the configuration $s^x p^y$, and obtain the charge density and potentials. Next, we proceed with the superposition scheme. Figure 3 shows the shape of the charge density for an AlAs/GaAs(110) interface between two model solids. For plotting purposes, we have averaged the charge density in planes parallel to the interface in a fashion similar to the potential in Eq. (1). Note that, within the model, there is a certain amount of "spillover" between the charge densities in the region near the interface, with tails of the wave function from AlAs extending into the GaAs and vice versa. This reflects the fact that we do not model the interface by a discontinuous charge density, but rather a smooth variation over a region of atomic dimensions, which is expected to closely mimic the situation at a real interface. The main difference between

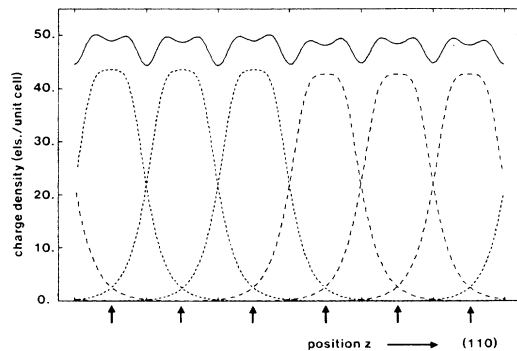


FIG. 3. Superposition of atomic charge densities to form a model solid interface. We show the plane-averaged charge density for pairs of GaAs (on the left, dotted lines) and AlAs atoms (on the right, dashed lines) in (110) planes. The units are (electrons/unit cell), for a supercell with 48 electrons. The arrows indicate the positions of the atomic planes. The solid line represents the superposition, which corresponds to the charge density in the model solid. Notice that the model solid is *not* cut off abruptly at the plane of the interface.

the model solid and the self-consistent charge density is that in the real solid some charge is drawn away from the regions near the atoms and piled up in the bonds. The qualitative aspect of the charge distribution near the interface is fairly well represented by the model solid, however.

Next, we evaluate the integral in Eq. (4). From that equation, it also follows that the average ionic and Hartree potentials are proportional to Ω^{-1} . Using the values of the volume of the unit cell in AlAs and GaAs, and summing over the two atoms in the bulk unit cell, we can derive the average potentials. Choosing the $l=1$ angular momentum component, as before, this leads to the following values of $(\bar{V}^{\text{ion}, l=1} + \bar{V}^H)$: -7.82 eV for GaAs, and -8.08 for AlAs. The exchange and correlation contributions to the average potentials are $\bar{V}_{\text{GaAs}}^{\text{xc}} = \bar{V}_{\text{AlAs}}^{\text{xc}} = -8.71$ eV. Finally, we add up the contributions for the individual materials, and find the shift in the total potential on either side of the interface: $\bar{V}_{\text{GaAs}} - \bar{V}_{\text{AlAs}} = (-16.53 \text{ eV}) - (-16.79 \text{ eV}) = 0.26 \text{ eV}$. This is to be compared with the value obtained from the full self-consistent calculations on the interface, using the supercell technique: $\Delta\bar{V} = 0.03 \text{ eV}$. The deviation here is actually larger than it will be in most other cases. Once we know $\Delta\bar{V}$, we can line up the band structures of materials, which are obtained from self-consistent bulk calculations. These band structures are significantly more accurate than those which would correspond to a model solid of superimposed atomic charge densities. We will assume that they are referred to the average electrostatic potential that we calculated for the model solid. Since the charge density of the model solid is not quite the same as that in the real bulk, the corresponding average potential can only be an approximation to the actual quantity. The model solid, however, enables us to obtain this average electrostatic potential on an absolute scale, and we will see by examining the results that the approximation is a good one. We have specified above the conventions which are used in deriving such a value; it is uniquely defined by the choice of pseudo-potential, local-density approximation, and atomic configurations.

We have studied a variety of other lattice-matched (110) interfaces. The configurations³⁵ that were used in the free-atom calculations are listed in Table I, and the results for ΔE_v (including spin-orbit splitting) are given in Table II. For lattice-matched systems, the model solid approach will yield the same value for the band alignment, irrespective of the interface orientation. This corresponds to what we found above from the self-consistent interface calculations on GaAs/AlAs. Table II only contains results for the (110) orientation. For interfaces between a group-IV element and a III-V or II-VI compound, or between compounds which do not have any elements in common, the (110) orientation is the only one which avoids charge accumulation without the need for mixing at the interface.²⁷ It has been shown⁹ that for polar interfaces different types of mixing can lead to different dipoles at the interface, which significantly alter the band lineups. This effect cannot be described by the present model solid approach, in which the neutral spheres cannot generate any net dipole across the interface, and it is clearly beyond the scope of *any* theory²⁻⁶ which assumes the dipole to be fixed by

consideration of the bulk alone. Other limitations of the model solid approach will be discussed in the next section.

V. DISCUSSION

A. Comparison with experiment

In Table II, we also list experimental data from various sources. At the present time, not all of these values are equally reliable. A striking example is that of the GaAs/AlAs interface, for which “Dingle’s 85/15 rule”³⁶ had become widely accepted: $\Delta E_v = 0.15\Delta E_g$, where ΔE_g is the difference in direct band gaps. Since last year, however, this value has been challenged and new results now indicate that more than 30% of the discontinuity is in the valence band.^{37–42} This example shows that even for this most widely used heterojunction the correct value could only be established by performing many experiments on high-quality interfaces, using a variety of different techniques. Since most of the heterojunctions listed in Table II have not received such careful attention, one should be very cautious when referring to these reported valence-band discontinuities.

We will attempt to give a brief overview of the experimental techniques which, at present, we regard to be the most reliable ones for deriving the band offsets, and illustrate them by references to work on GaAs/AlAs. Photoluminescence experiments on quantum wells can give very accurate results, but should be limited to cases in which the band offsets can be derived without having to rely on the precise knowledge of additional quantities, such as effective masses or exciton binding energies. Structures in which a crossover of bands can be observed are most appropriate, e.g., in the AlGaAs/AlAs heterojunctions as a function of composition³⁸ or pressure.²⁹ I-V and C-V measurements may or may not be reliable, depending on the system and the procedure used. The reason is that heterojunctions often contain charges at or near the interface, which may cause significant band bending. One should therefore either eliminate these charges,³⁹ or use a measurement procedure that is insensitive to these effects, such as C-V profiling through the junction.⁴⁰ A promising new approach is that of charge-transfer measurements at single heterojunctions⁴¹ or in modulation-doped superlattices.⁴² Finally, we have noticed that photoemission spectroscopy, while in principle providing a direct measurement of the valence-band discontinuity, has produced widely varying results by different groups for the same system. A possible reason is the technological difficulty involved in producing high-quality epitaxial interfaces. Measurements on lower-quality heterojunctions can lead to a ΔE_v value which is not representative of an ideal system. For a more detailed evaluation of current experimental techniques, we refer to the critical review by Duggan.³⁷

For GaAs/AlAs, our model solid result is very close to the present experimental value; closer, indeed, than the self-consistent calculation. Another very interesting case is that of InAs/GaSb, in which experimentally a “broken-gap lineup” was detected,⁴³ meaning that the conduction band in InAs is lower in energy than the

valence band in GaSb. From the self-consistent interface calculations, we find that $\Delta E_v = 0.38$ eV. The band gap of InAs is 0.41 eV at 0 K, and 0.35 eV at room temperature,²⁵ which means that the conduction band of InAs almost lines up with the valence band of GaSb. This result is close to that obtained from an earlier self-consistent calculation on a InAs/GaSb(100) interface.⁴⁴ The model solid result for ΔE_v is 0.51 eV, which even more clearly leads to a “broken gap” lineup.

B. Comparison with other model theories

In Table II, we have also given results from a number of other models. We should point out that these numbers [for Harrison’s theory, the linear muffin-tin orbitals (LMTO) calculations, and Tersoff’s approach] do not include spin-orbit splitting. However, as we have remarked before, these corrections are usually smaller than 0.05 eV. We will briefly describe these models here, and point out similarities and differences with our model solid approach. We will discuss the electron affinity rule,² the Frenley-Kroemer theory,³ Harrison’s theory of natural band lineups,⁴ and the model developed by Tejedor and Flores,⁵ and independently by Tersoff.⁶ We will also devote some attention to a line-up scheme that occurs naturally in the context of LMTO calculations.⁴⁵

Our model solid approach is in spirit related to the electron affinity rule,² in that it derives the band discontinuities as a difference between quantities which are defined for each semiconductor individually. In the case of electron affinities, the problem is that these quantities are measured experimentally for a specific surface, and therefore depend on orientation, relaxation, reconstruction, etc., which can all introduce extra dipoles that shift the energy bands in the bulk. One could try to define an “electron affinity” which would only take the “intrinsic” contribution due to the bulk into account, and ignore the surface effects. Van Vechten⁴⁶ has argued that such quantities would predict the lineups reliably. The main problem with such an approach is that the separation between the bulk and the “surface” part is not unique, so that it is not clear how to derive an “intrinsic electron affinity” from experimental information alone.

Our model solid approach defines a reference level corresponding to a well specified “model surface,” which, by construction, cannot introduce any “extra dipoles.” The reference potential can therefore in principle be considered to be a quantity intrinsic to the bulk material (its actual value being determined by the conventions regarding pseudopotentials and configurations that we specified above). Furthermore, the fact that the results are so close to those from self-consistent calculations shows that this model provides a good description of the charge distribution at the heterojunction. Since we do not allow any *additional* charge rearrangement, we should always expect some deviation between the model solid results and the full self-consistent calculations. The comparison of our results for valence-band offsets shows that these deviations are fairly small, however.

Additional dipoles may be due to several different sources. Displacements of atoms around the interface

may in certain cases set up dipoles which shift the energy levels. We have argued that at (110) interfaces the deviations from the ideal structure will be small, and will have small effects on the lineups. In some cases, like ZnSe/Ge, however, the sizable difference in ionicity may introduce more significant displacements, and consequently larger dipoles. Also, we do not consider the model to be applicable to polar interfaces. As explained above, additional dipoles which depend on the type of mixing at the interface can occur in such cases.

Small deviations from our model may also be caused by the fact that we are using *neutral* atoms as our building blocks. Use of charged objects, however, would destroy the simple, "dipole-free" picture of the reference surface that our superposition of neutral atoms provides. Frenseley and Kroemer have actually constructed a model in which they superimposed spherical ions to construct the solid.³ They chose the mean interstitial potential in the diamond or zinc-blende structure as the electrostatic reference potential for each semiconductor. If the crystal were viewed as a superposition of spherical charges, this reference potential would correspond to the vacuum potential, provided the charges were so localized that the charge density in the interstitial region was negligible. These potentials were then lined up, taking a dipole shift into account, which was expressed in terms of charges on the atoms, and subsequently in terms of electronegativity differences. It turned out that these dipole shifts were quite small in most cases, indicating that the intrinsic lineups should be close to the true result. We came to the same conclusion in the present work, using a better justified value for the intrinsic potential.

Frenseley and Kroemer used empirical pseudopotentials to generate values for the reference potentials. To really test how good this procedure is, one should use the better quality pseudopotentials which are available nowadays, as we have done in our studies. Since we had the results from bulk calculations at our disposal, we could examine the potential values in the interstitial regions. It turned out that the values we obtained (without the dipole correction) were quite different from Frenseley and Kroemer's original results, and also different from the results from self-consistent interface calculations (by more than 0.25 eV, on the average). We assumed that the qualitative result that the additional dipole shifts are small remains valid, such that these corrections would not significantly affect the lineups; in any case, adding the dipole shifts suggested by Frenseley and Kroemer made the agreement with our values even worse. Inspection of the potential in the interstitial region showed us why the results would not be reliable. We found that the potential does not really flatten out near the interstitial site, as Frenseley and Kroemer assumed, and still shows significant structure. This is true both for elemental and compound semiconductors. Under these circumstances, it is hard to determine what the appropriate value for the reference potential is; is it the value at the interstitial point itself, or an average over some region? This can make a difference of up to 1 eV. Frenseley and Kroemer themselves acknowledged that their electrostatic potential inside the interstices of the diamond structure was only flat within about 1 eV.⁴⁷ To

make things worse, it turned out that the value of the potential at the interstitial point was only converged at a much higher cutoff than we needed for the other aspects of our calculations (e.g., larger than 18 Ry for Si). This would require one to do the bulk calculation with a much higher accuracy than is typically required for deriving energy eigenvalues. This is to be expected, if one insists on deriving an accurate value at one point, instead of dealing with averaged quantities, or properties which depend only on the total charge density. We therefore conclude that the Frenseley-Kroemer scheme *in principle* offers a very attractive approach, but turns out to be unsuitable for generating accurate values for the lineups.

Our approach has in common with Harrison's theory of natural band lineups⁴ that a reference energy level for each material is derived from atomic information. However, a key difference should be emphasized: Harrison's model was based on the atomic term values, which he assumed to carry over from atom to solid. This is clearly different from our model solid approach, in which all electronic energy levels are shifted by the superposition of atomic potentials. This choice to define the average potential of the model solid is better justified by self-consistent calculations and seems to be in better agreement with experiment. Harrison has recently developed a new point of view, which is closely related to Tersoff's approach, but applied in a tight-binding context.⁴⁸ Here, the averaged hybrid energy is identified as the "neutrality level," that will be pinned at a heterojunction. Values from both the "natural band lineup" scheme and the new "pinned" theory are given in Table II. It is not clear to what extent this new method actually improves the natural band lineups. It might be that the tight-binding formalism, while very appealing because of its simplicity and generality, is not accurate enough to predict values on a scale that is necessary for these applications.

Another scheme which establishes an absolute energy reference level for tetrahedral semiconductors has been developed in the context of the LMTO all-electron method, by Vergés *et al.*,⁴⁵ and Christensen and Andersen.⁴⁹ They were interested in deriving absolute deformation potentials for individual semiconductors, but their approach can also be used to line up band structures of pairs of different semiconductors. Their reference level is the zero of electrostatic potential in the infinite crystal, as evaluated with the atomic-spheres approximation, i.e., with point charges placed at the atomic and tetrahedral interstitial sites. This turns out to be a reasonable *ansatz* for deriving the band lineups. Values for ΔE_v obtained by this approach are listed in Table II.

The last source of additional dipoles to be discussed here is due to screening effects, of the type that play the dominant role at a metal-metal interface. Such dipoles are clearly not present in our model solid approach, which is therefore not applicable to metallic interfaces or Schottky barriers. Tersoff,^{6,50,51} and before him Tejedor and Flores,⁵ have argued that such screening will also be the dominant effect that determines the lineups at a semiconductor-semiconductor interface: dipoles will be set up which will drive the system towards alignment of the "neutrality levels" of the materials (as would be the

case at the junction between two metals, where the Fermi levels line up). Although this picture seems to be contrary to the assumptions that underlie the model solid approach, the two points of view may actually be not that far removed from one another. We have remarked before that the superposition of atomic charge densities effectively deals with a model surface for which there is significant overlap of the charge densities, with the tails of the bulk charge density of one material sticking out into the other side. This charge distribution may actually incorporate much of the dipole that Tejedor and Flores and Tersoff consider to be the dominant effect.

It is essential to point out, in this context, that the concept of “dipole” at an interface is not uniquely defined—its magnitude depends on the choice of “reference surfaces” that are brought together to create an interface within a specific model. It is therefore possible for different models to obtain good results, while claiming to deal with dipoles of very different magnitude. The reference surfaces that we have chosen here are clearly a good “ansatz:” the “additional dipoles,” due to charge redistribution at the interface are small. Tejedor and Flores and Tersoff do not need to make an ansatz for the charge density since they consider only the final lineup that the system would attain *if* the screening effects were as strong as they are at a metal/metal interface. We can recognize two problems with this approach. First, assuming that a unique neutrality level exists, no convincing evidence has been given so far that the induced dipoles are actually strong enough to drive the system towards the “neutral” lineup. Second, the assignment of a neutrality level to each material is not straightforward. Tersoff has suggested two possibilities: a simple average of the indirect gap,⁵⁰ or a branch point derived from a Green’s-function approach;^{6,51} neither of these is rigorous. The Green’s-function approach itself involves a number of approximations and assumptions.⁵¹ For instance, a specific choice of orientation has to be made in the Green’s function $G(\mathbf{R}, E)$, and only the $\langle 110 \rangle$ direction produced reasonable results. Also, the branch point energy E_b depends on the value of \mathbf{R} . Still, the success of the theory clearly depends on how accurately these numbers can be generated, and it may be somewhat fortuitous that the particular choice that was made produces values that are reasonably close to the self-consistent results.

From this overview, it should be clear that none of the model theories is able to adequately deal with *all* effects of electronic rearrangement at the interface. Our superposition of atomic charge densities model is the only one which is based upon, and has been directly compared with, results from self-consistent interface calculations. This places our approach on a strong footing, particularly since the values we obtain are so close to the self-consistent results.

VI. CONCLUSIONS

We have described our first-principles approach to deriving band offsets at semiconductor interfaces. Density-functional theory and *ab initio* pseudopotentials were used to perform self-consistent calculations, and derive valence-band discontinuities for a large number of

lattice-matched interfaces. The calculations were illustrated with the example of a GaAs/AlAs interface, and we presented an analysis of the sensitivity of our results to the procedures used; the numerical precision is on the order of 0.05–0.10 eV. Values for valence-band discontinuities were summarized in Table II. We also listed reported experimental values in that table; we have pointed out which measurements we consider reliable, and have given a critical overview of the available experimental techniques.

Our systematic analysis has allowed us to draw some general conclusions: for suitably chosen heterojunction systems, the lineups are independent of orientation, and they obey the transitivity rule. This indicates that the offsets can be described by a linear theory, in which the lineups are obtained as the *difference* between quantities which are *intrinsic* to each material. To establish the reference levels for each solid, we constructed a model based on superposition of (pseudo)atomic charge densities. The average (pseudo)potential in such a model solid can be derived from atomic calculations; the atomic configurations were taken from tight-binding theory to simulate as well as possible the solid. This uniquely defines the reference potentials. The band structures obtained from self-consistent bulk calculations are then aligned according to these reference levels. The resulting lineups are close to those obtained from full self-consistent interface calculations, and to reliable experimental values. We consider this to be evidence that our *ansatz* is close to the real situation at the interface. Extra dipoles may be present in certain cases; however, in the cases studied these amount to only small corrections, and at this point we believe there is no simple universal theory that describes the exact screening mechanism.

We have also discussed the relationship with other model theories. In particular, we compared our approach to Tersoff’s theory, which seems to produce good results, even though it relies on certain untested assumptions, and the prescription for finding the reference level is not rigorous. The advantages of our superposition of neutral atomic charge densities are that it provides a well defined, physical model, that the numerical work is straightforward, and that, even though it should only be considered as an *ansatz*, the results are close to those obtained from self-consistent interface calculations.

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