

# Effect of spin-orbit interaction on heterojunction band discontinuities

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The effect of spin-orbit interaction is included in the linear combination of atomic orbitals calculation of heterojunction band discontinuities. It is found that spin-orbit interaction is not negligible when the atomic number of the constituent atoms exceeds about 40. The effect of spin-orbit interaction as well as some interesting observations and their implications are briefly discussed.

The energy band discontinuities at the interface of a semiconductor heterojunction play an important role in determining the electronic properties of heterostructure devices. Many theoretical techniques<sup>1</sup> have been applied to calculate the band-edge discontinuities at the heterointerface. Unfortunately, the results of the various attempts have not been conclusive. Nevertheless, Harrison's<sup>2</sup> tight binding approach has received much attention due to its simplicity, predictive power, and apparent success.<sup>1</sup> However, despite its success and ability to predict trends of interfaces of the same family in III-V and II-VI compounds on Ge systems, there exist discrepancies between theory and experiment,<sup>3</sup> especially when the compound semiconductor contains a heavy anion ( $Z \gtrsim 40$ ). In this work, the effect of spin-orbit interaction is included in the linear combination of atomic orbitals (LCAO) method. It is found that the spin-orbit interaction is not negligible when the compound semiconductor contains a heavy atom ( $Z \gtrsim 40$ ).

There have been some efforts to incorporate the spin-orbit interaction in LCAO models,<sup>4-6</sup> most notably the work of Chadi.<sup>6</sup> However, Ref. 6 neglects the spin-orbit contribution between adjacent atoms, which is included in the present work. The results of Refs. 2, 6, and the present work are tabulated for comparison.

The LCAO theory formulated by Harrison is based on the calculation of valence band energies by Chadi and Cohen<sup>7</sup> which, in turn, is an application of the LCAO method of Slater and Koster.<sup>8</sup> The spin-independent Hamiltonian has eight quantum states of  $s$ ,  $p_x$ ,  $p_y$ , and  $p_z$ , for the anion and cation. We have included the effect of spin-orbit coupling by forming a new Hilbert space from the direct product of the old Hilbert space with a spin space  $\{\alpha, \beta\}$ . Thus, the sixteen basis functions are given by

$$\psi_i = (s, p_{x,y,z})^{a,c} \times \{\alpha, \beta\},$$

where the superscripts  $a$  and  $c$  refer to the anion and cation, respectively, and the subscript  $i$  runs from 1 to 16.

The spin-dependent Hamiltonian is given by

$$H = H_0 S_0 + \sum_j \xi(\mathbf{r} - \mathbf{r}_j) \mathbf{L}_j \cdot \mathbf{S}_j,$$

where

$$\xi(\mathbf{r}) = \frac{1}{2m^2 c^2 r} \frac{dV}{dr}.$$

In the above,  $H_0$  is the  $8 \times 8$  spin-independent Hamiltonian

diagonalized by Chadi and Cohen,<sup>7</sup>  $S_0$  is the  $2 \times 2$  identity matrix, and  $V$  is the potential. The above results in a  $16 \times 16$  matrix which can then be block diagonalized and solved at zone center ( $k = 0$ ). The new  $16 \times 16$  matrix has a completely different form from the  $8 \times 8$  as many matrix elements remain nonzero due to the spin-spin couplings. However, the  $s$  and  $p$  blocks can be separated, and only the  $p$  blocks are retained as we are interested in the valence band states. This leaves us with  $12 \times 12$  matrix, the lowest two eigenvalues of which give the top of the valence and split-off bands. Assuming that the coupling between  $p_x$ ,  $p_y$ , and  $p_z$  states are identical, the matrix is further reduced to one which contains three  $4 \times 4$  blocks given by

$$\begin{pmatrix} E_a + \Delta_a & \Delta_a(1-i) & \Delta_{ac} - V_{xx} & \Delta_{ac}(1-i) \\ \Delta_a(1+i) & E_a + \Delta_a & \Delta_{ac}(1+i) & \Delta_{ac} - V_{xx} \\ \Delta_{ac} - V_{xx} & \Delta_{ac}(1-i) & E_c + \Delta_c & \Delta_c(1-i) \\ \Delta_{ac}(1+i) & \Delta_{ac} - V_{xx} & \Delta_c(1+i) & E_c + \Delta_c \end{pmatrix}$$

where  $E_a$ ,  $E_c$  are the  $p$ -state energies on the atomic anion and cation, and  $\Delta_a$ ,  $\Delta_c$  are the spin-orbit splitting of the anion and cation, respectively;  $V_{xx}$  is the interatomic matrix element between  $p$  states of adjacent atoms and is given by  $V_{xx} = 2.16 \hbar^2 / md^2$ , where  $d$  is the bond length, and  $\Delta_{ac}$  is a coupling term to be determined. The characteristic equation of the matrix is then solved by adjusting  $\Delta_{ac}$  until the difference between the lowest two eigenvalues agree with the known spin-orbit splitting  $\Delta$  of the semiconductor. Table I compares the top of the valence band calculated from the

TABLE I. Comparison of the values of the top of valence band. The second column lists values calculated from Eq. (12) of Ref. 6, and the third column are those obtained with the present formulation. The fourth column lists the coupling term  $\Delta_{ac}$  and the last column lists the spin-orbit splitting. All values listed are in eV.

	Harrison	Chadi	This work	$\Delta$
InP	9.64	9.70	9.55	0.11
AlAs	9.57	9.67	9.54	0.28
GaAs	9.53	9.65	9.49	0.34
InAs	9.21	9.35	9.15	0.39
AlSb	8.67	8.90	8.80	0.75
GaSb	8.69	8.94	8.85	0.80
InSb	8.41	8.69	8.61*	0.81
CdSe	10.35	10.50	10.42	0.53

\* This value is only an estimate.

above matrix with those of Refs. 2 and 6 [using Eq. (12) of Ref. 6]. Since the spin-orbit splitting can be obtained from the empirical expressions

$$\Delta \approx \frac{1}{4} \Delta_c + \frac{3}{4} \Delta_a,$$

$$\Delta \approx \frac{1}{3} \Delta_c + \frac{2}{3} \Delta_a,$$

for III-V and II-VI compounds, respectively, the influence of the anion is expected to be greater. As can be seen from Table I, for materials with heavy elements, the effect of spin-orbit interaction is not negligible.

From the calculated (Table I) values of the top of the valence band, we can determine the valence (and hence conduction) band energy discontinuities. Table II lists the calculated valence band discontinuities and compares the theoretical values with experimental results.<sup>3</sup> Here, it is apparent that the inclusion of spin-orbit interaction in compounds which contain heavy elements improves considerably the agreement between theory and experiment under the present formulation. Table III lists the calculated discontinuities for some lattice-matched systems. It is apparent that the spin-orbit interaction cannot be neglected when the constituent elements include a heavy atom, as the results for Sb would indicate. The effect of spin-orbit interaction would be greater for Te compounds.

The LCAO theory neglects any local microscopic effects and differences in bond lengths  $d$  of the constituent semiconductors. As a result, the best accuracy is obtained for lattice-matched systems. For lattice-mismatched systems, local rearrangement of atoms is expected, and the "effective" bond length will be different from the bulk values. Also, the local structural configuration near the interface will probably depend on the growth conditions and crystal orientation, and different experimental results of the band discontinuity for the same semiconductor pair can be expected. Precise calculation of the band discontinuity will probably require detailed knowledge of the chemical as well as structural arrangement of the interfacial atomic layers. Therefore, for accurate prediction of band discontinuities, the LCAO method should only be used for lattice-matched systems. From Table II, it can be seen that inclusion of the spin-orbit effects has decreased the difference between calculated and experimental values. The "remaining" discrepancy can be attributed to the difference in bond lengths and other related local structural and electronic effects. Though the effect of the spin-orbit interaction is shown here for the LCAO calculation, its importance for systems with heavy elements is not restricted to this method only, and should be included in other theoretical methods, including the self-consistent pseudopotential approach.

TABLE II. Valence band discontinuities of III-V and II-VI compounds on Ge.

	Harrison	Chadi	This work	Experiment
InSb-Ge	-0.71	-0.72	-0.48	0.1
GaSb-Ge	-0.43	-0.47	-0.24	0.15
InAs-Ge	0.09	-0.06	0.06	0.0
InP-Ge	0.52	0.29	0.46	0.50

TABLE III. Valence band discontinuities of lattice-matched heterojunctions.

	Harrison	Chadi	This work	Experiment
InP-CdS	1.48	1.47	1.56	1.63
InAs-CdSe	1.14	1.15	1.27	...
GaSb-AlSb	-0.02	-0.04	-0.05	...

An interesting observation depicted in Fig. 1 is that when the atomic number of the cation is  $\leq 40$ , the energies of the split-off and valence bands are approximately the same for systems with common anions. Thus, the split-off band is almost continuous across the interface. The insert (from Ref. 9) of Fig. 1 shows the interesting comparison with the anion rule of Schottky barriers, which states that the Schottky barrier for holes on common III-V and II-VI semiconductors contacted by Au depends only on the anion.<sup>9</sup> In the insert, the triangles are the valence band maxima for III-V and II-VI compounds with common anions, and the vertical lines are the maxima of the split-off bands. Here the split-off band energies of different III-V compounds are also approximately equal. This seems to indicate that a rough estimate of the valence band discontinuities can be obtained from Schottky barrier data in the limit that the thickness of the metallic gold tends to zero. This implies that the valence band discontinuity at the heterojunction of compounds with the same anion is small, in agreement with the LCAO results.

The extremely small discontinuity in the split-off bands for III-V compounds has implications on calculations involving the split-off bands (e.g., nonradiative Auger recom-

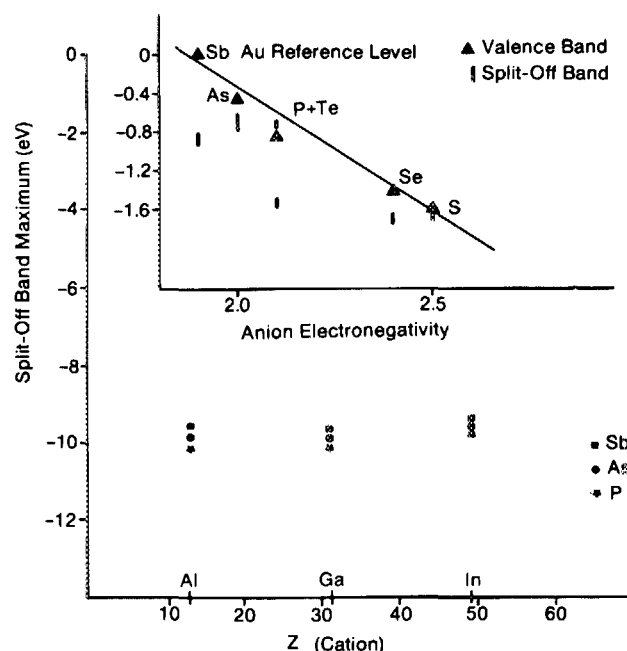


FIG. 1. Top of the split-off band energy vs the atomic number of the cation. The insert plots the top of the valence band energy vs the anion electronegativity. The vertical lines denote the top of the split-off band.

bination, intervalence band absorption, impact ionization, etc.) in quantum well and superlattice structures. A continuous band would alter the nature of the density of states and the dynamical properties of the split-off holes.

In summary, band discontinuities of heterojunctions have been estimated from the LCAO method including the effect of spin-orbit interaction. The results show that spin-orbit interaction is not negligible when the atomic numbers of the constituent atoms exceed about 40.

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