Strong Linear-k Valence-Band Mixing at Semiconductor Heterojunctions

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This paper examines linear-**k** terms in the Γ_8 valence-band Hamiltonian for heterostructures of zinc-blende-type semiconductors. In bulk crystals such terms are known to be extremely small, due to their origin as relativistic perturbations from d and f orbitals. However, in heterostructures there is a nonvanishing contribution from p orbitals. This contribution is an order of magnitude larger than the corresponding bulk term, and it should give rise to an optical anisotropy comparable to (although smaller than) that seen in recent experiments on the quantum-well Pockels effect.

The discovery of the quantum-well Pockels effect by Kwok *et al.* [1] has attracted considerable interest in the semiconductor physics community over the past several years [2–8]. This effect involves a dramatic increase in optical anisotropy caused by the reduction in crystal symmetry (from T_d to C_{2v}) at a heterojunction between two zinc-blende-type semiconductors. It is now widely accepted that in type-I systems, the quantum-well Pockels effect is primarily a consequence of the mixing of light and heavy holes that arises from the rapid change in crystalline potential at an abrupt junction. Such microscopic interface effects can be described simply by adding a δ-function potential to the standard valence-band envelope-function Hamiltonian [3,5,9–12].

It is, of course, well known that linear-**k** mixing of the Γ_8 valence states [13–17] must also contribute to the Pockels effect. However, apart from a few early studies [2,18] (which appeared before the significance of interface-induced mixing was known), linear-**k** mixing has been neglected in all theoretical models of the quantum-well Pockels effect. This is because there is universal agreement that such mixing is far too weak to account for the observed optical anisotropy in quantum wells. Indeed, the neglect of linear-**k** mixing is so common that it has become an automatic first step in almost all valence-band calculations.

In this paper it is shown that, although the bulk mixing is indeed very small [19], linear-**k** valence-band mixing is greatly enhanced in the vicinity of a heterojunction. The Γ_8 linear-**k** mixing at an interface is an order of magnitude larger than in the bulk, and it should yield an optical anisotropy comparable to (but smaller than) that observed experimentally. (This conclusion is based on a comparison of the present Hamiltonian with similar Hamiltonians used in earlier studies; no optical spectra are calculated here.) Therefore, this source of mixing should be included in theoretical models of the quantum-well Pockels effect. It may or may not be significant in other situations, but the neglect of such mixing should no longer be considered automatic.

The reason why interface linear-**k** mixing is so much larger than bulk mixing can be understood from simple symmetry arguments. Linear-**k** terms in the Γ_8 Hamiltonian arise to lowest order as second-order perturbations involving one matrix element of the spin-orbit interaction and one matrix element of the **k** · **p** interaction [14,15]. In the bulk, this coupling occurs via states of symmetry Γ_3 and Γ_5 (in the notation of Ref. [13]), which are derived primarily from atomic d and f orbitals, respectively. As discussed by Cardona *et al.* [16,17], f orbitals are not available in the core states of common semiconductors, and the excited Γ_5 states are very high in energy. Therefore, the main contribution to Γ_8 bulk mixing is from the uppermost d states in the atomic cores.

However, as shown below, coupling to the p-like Γ_4 states is not forbidden by symmetry; it just so happens that the contributions from this coupling to the Γ_8 Hamiltonian have equal magnitude and opposite sign, so they cancel out in the bulk. But in a heterostructure, these terms have *different operator ordering* with respect to the crystal-momentum operator $\mathbf{k} = -i\nabla$, so the contribution from Γ_4 states does not vanish. The data given in Refs. [16] and [17] show that the momentum matrix elements coupling the Γ_4 valence states to other Γ_4 states are typically a factor of 4 larger than those involving d core states, while the corresponding energy gaps are a factor of 4 smaller. Thus, one can easily see how the Γ_4 contribution would tend to dominate that from Γ_3.

The same point was raised in another context by Kane [14, pp. 95–96], who noted that the smallness of the Γ_8 linear-**k** Hamiltonian is an abnormal situation caused by the lack of any contribution from p-like states. At lower symmetry points such as X and L, the p-like states do contribute, and the spin-orbit-induced linear-**k** terms are much larger. The present work shows that the reduced symmetry at a heterojunction has the same basic effect.

The linear-**k** Hamiltonian for Γ_8 and Γ_7 valence electrons in heterostructures is derived here using Burt's exact envelope-function formalism [20]. In this theory, the microscopic Schrödinger equation for the heterostructure is treated exactly using the Luttinger-Kohn representation [21], and a set of approximate effective-mass equations is derived systematically by discarding contributions that (under suitable conditions) can be proven to be negligible. This yields a well-justified envelope-function Hamiltonian

with a clearly defined ordering of operators. The same approach was used earlier to treat k^2 terms in the valence-band Hamiltonian [22], and the results show good agreement with tight-binding calculations [23].

The only difference between the present work and Burt's derivation [20] is the inclusion of an extra perturbation—namely, the spin-orbit Hamiltonian $H_{so} = \boldsymbol{\sigma} \cdot \mathbf{S}$, in which $\boldsymbol{\sigma}$ is the Pauli spin matrix vector and [14]

$$\mathbf{S} = \frac{\hbar}{4m^2c^2}(\nabla V \times \mathbf{p}), \tag{1}$$

where V is the potential energy of the electron and $\mathbf{p}$ is its momentum. As in the bulk case [14,15], H_{so} is treated using second-order perturbation theory, with the terms of interest being first order in both H_{so} and $\mathbf{k} \cdot \mathbf{p}$. The details of the derivation are precisely the same as in Burt's paper [20], so they will not be repeated here; the result is simply an extra term in the envelope-function Hamiltonian of the form

$$W_{ns,n's'} = \frac{1}{m} \sum_{\alpha,\beta} \sigma_{ss'}^\beta \sum_{n''} [k_\alpha (p_{nn''}^\alpha S_{n''n'}^\beta \omega_{nn''}^{-1})$$
$$+ (S_{nn''}^\beta p_{n''n'}^\alpha \omega_{nn''}^{-1})k_\alpha]. \tag{2}$$

Here n is an index labeling the orbital part of the basis functions, while $s = \pm$ labels the sign of the z component of the spin; α and β are Cartesian coordinate indices, with $k_\alpha = -i\partial/\partial x_\alpha$. The terms $p_{nn'}^\alpha$ and $S_{nn'}^\beta$ are matrix elements of the operators p^α and S^β, and $\omega_{nn'} = (E_n - E_{n'})/\hbar$, where E_n is the energy of state n. In the derivation of Eq. (2) it was assumed that $E_n = E_{n'}$.

It should be noted that the matrix elements in Eq. (2) are bulklike parameters with a step-function dependence at a heterojunction. The microscopic interface effects treated in Refs. [5] and [20] are not considered here.

The valence states of interest are labeled X, Y, and Z; these states are derived primarily from p orbitals and belong to the Γ_4 representation. To see which states n'' contribute to Eq. (2), note that the vector $\mathbf{p}$ belongs to Γ_4, with $\Gamma_4 \times \Gamma_4 = \Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5$, while the pseudovector $\mathbf{S}$ belongs to Γ_5, with $\Gamma_4 \times \Gamma_5 = \Gamma_2 + \Gamma_3 + \Gamma_4 + \Gamma_5$ [13]. Therefore, intermediate states of symmetry Γ_3, Γ_4, and Γ_5 are permitted in Eq. (2). These give rise to three independent real constants:

$$C_3 = \frac{1}{m} \sum_n^{\Gamma_3} \frac{p_{Xn}^x S_{nZ}^z}{\omega_{Xn}}, \tag{3}$$

$$C_4 = \frac{1}{m} \sum_n^{\Gamma_4} \frac{p_{Xn}^y S_{nX}^y}{\omega_{Xn}}, \tag{4}$$

$$C_5 = \frac{1}{m} \sum_n^{\Gamma_5} \frac{p_{Xn}^y S_{nX}^y}{\omega_{Xn}}. \tag{5}$$

Terms also arise that are proportional to

$$C_3' = \frac{1}{m} \sum_n^{\Gamma_3} \frac{p_{Xn}^x S_{nX}^x}{\omega_{Xn}}, \tag{6}$$

but it turns out that $C_3' = 0$, because S^x changes sign under the reflection $(xyz) \rightarrow (xzy)$.

Upon evaluating Eq. (2) for each of the Γ_4 valence states, one finds the following results:

$$W_{X\pm,X\pm} = \mp 2\{(C_4 + C_5)k_z\},$$
$$W_{X\pm,X\mp} = \mp i2\{(C_4 + C_5)k_y\},$$
$$W_{Y\pm,Y\pm} = \pm 2\{(C_4 + C_5)k_z\},$$
$$W_{Y\pm,Y\mp} = -2\{(C_4 + C_5)k_x\},$$
$$W_{Z\pm,Z\pm} = 0,$$
$$W_{Z\pm,Z\mp} = 2\{(C_4 + C_5)k_\pm\},$$
$$W_{X\pm,Y\pm} = 0, \tag{7}$$
$$W_{X\pm,Y\mp} = C_3 k_y + k_y(-C_4 + C_5)$$
$$\qquad\qquad \pm i[k_x C_3 + (-C_4 + C_5)k_x],$$
$$W_{X\pm,Z\pm} = \pm[k_x C_3 + (-C_4 + C_5)k_x],$$
$$W_{X\pm,Z\mp} = -[C_3 k_z + k_z(-C_4 + C_5)],$$
$$W_{Y\pm,Z\pm} = \mp[k_y C_3 + (-C_4 + C_5)k_y],$$
$$W_{Y\pm,Z\mp} = \mp i[C_3 k_z + k_z(-C_4 + C_5)],$$

where $k_\pm = k_x \pm ik_y$ and $\{AB\} = \frac{1}{2}(AB + BA)$. Note that the operator ordering obtained from Γ_3 states is opposite to that associated with Γ_4 and Γ_5.

Of course, in addition to the second-order terms (7), there is a first-order spin-orbit splitting $\Delta_0 = -i3S_{XZ}^y$. One can diagonalize the latter by transforming to the $|j, m\rangle$ basis [22]

$$|\tfrac{3}{2}, +\tfrac{3}{2}\rangle = \tfrac{1}{\sqrt{2}}(|X+\rangle + i|Y+\rangle),$$
$$|\tfrac{3}{2}, -\tfrac{3}{2}\rangle = \tfrac{1}{\sqrt{2}}(|X-\rangle - i|Y-\rangle),$$
$$|\tfrac{3}{2}, +\tfrac{1}{2}\rangle = \tfrac{1}{\sqrt{6}}(|X-\rangle + i|Y-\rangle - 2|Z+\rangle),$$
$$|\tfrac{3}{2}, -\tfrac{1}{2}\rangle = \tfrac{1}{\sqrt{6}}(-|X+\rangle + i|Y+\rangle - 2|Z-\rangle), \tag{8}$$
$$|\tfrac{1}{2}, +\tfrac{1}{2}\rangle = \tfrac{1}{\sqrt{3}}(|X-\rangle + i|Y-\rangle + |Z+\rangle),$$
$$|\tfrac{1}{2}, -\tfrac{1}{2}\rangle = \tfrac{1}{\sqrt{3}}(-|X+\rangle + i|Y+\rangle + |Z-\rangle).$$

In this basis, the linear-$\mathbf{k}$ Hamiltonian takes the form

$$W = \begin{bmatrix} 0 & \kappa_- & \lambda_+ & \mu_z & -2\nu_z \\ & 0 & \mu_z & \lambda_- & -2\nu_z & -\nu_- \\ & & 0 & \kappa_+ & 0 & \sqrt{3}\nu_+ \\ & & & 0 & \sqrt{3}\nu_- & 0 \\ \text{H.c.} & & & & 0 & 0 \\ & & & & & 0 \end{bmatrix}, \tag{9}$$

in which "H.c." stands for Hermitian conjugate and

$$\kappa_\pm = \tfrac{\sqrt{3}}{2}\{Ck_\pm\},$$
$$\lambda_\pm = \mp\tfrac{1}{2}\{Ck_\pm\} \pm [C_i, k_\pm],$$
$$\mu_z = \{Ck_z\} + [C_i, k_z], \tag{10}$$
$$\nu_\alpha = \tfrac{1}{2\sqrt{2}}(\{C'k_\alpha\} + [C_i, k_\alpha]).$$

Here $[A, B] = AB - BA$, and the constants C, C', and C_i are defined by

$$C = \tfrac{2}{\sqrt{3}}(C_3 + 2C_5),$$
$$C' = \tfrac{2}{\sqrt{3}}(C_3 - 3C_4 - C_5), \qquad (11)$$
$$C_i = \tfrac{1}{\sqrt{3}}(C_3 + C_4 - C_5).$$

C is the usual linear-$\mathbf{k}$ coefficient for Γ_8 bands [14,15], while C' is an analogous quantity that couples the Γ_8 states to the Γ_7 split-off band [24,25]. Both of these terms appear within symmetrized products, so they both contribute to the Hamiltonian in bulk material.

However, C_i appears only within the commutator $[C_i, k_\alpha] = i(\partial C_i/\partial x_\alpha)$. Therefore, the contribution from C_i is nonvanishing only in inhomogeneous media. At an abrupt heterojunction, $\partial C_i/\partial x_\alpha$ has the form of a δ-like function whose strength is equal to the change in C_i across the junction. From Eqs. (9) and (10) one sees that C_i couples the Γ_8 light and heavy hole states. The form of this coupling is mathematically the same as that generated by the abrupt change in potential at the interface [5,11], which is currently viewed as a primary source of optical anisotropy in the quantum-well Pockels effect [3,4,6,7].

The question is thus: Is the change in C_i sufficiently large to yield a significant anisotropy? The answer to this question hinges on the magnitude of C_4, which can be estimated by considering the contribution from the lowest-lying Γ_4 conduction states X', Y', and Z'. The relevant coupling constants [17] are the off-diagonal spin-orbit coupling $\Delta^- = -i3S_{XZ'}^y$, the momentum matrix element $Q = (i\hbar/m)p_{XZ'}^y$, and the Γ_4 energy gap $E_{g4} = E_{X'} - E_X$, in terms of which

$$C_4 \simeq \frac{Q\Delta^-}{3E_{g4}} = \frac{Q\Delta^-}{3E_0' + \Delta_0 + 2\Delta_0'}, \qquad (12)$$

where $E_0' = E_{\Gamma_7^c} - E_{\Gamma_8^v}$ and $\Delta_0' = -i3S_{X'Z'}^y$.

Unfortunately, data on Δ^- are rather sparse. A few values were given in Refs. [17] and [26], but these did not include any pairs of lattice-matched semiconductors. Therefore, the tight-binding model described in Ref. [17] is used here to estimate Δ^- for a variety of other semiconductors. The model is based on Harrison's [27] universal tight-binding parameters supplemented by Chadi's [28] tabulation of atomic spin-orbit splittings.

The Γ_4 valence and conduction states are expressed as

$$|X\rangle = (-|X_c\rangle - \eta|X_a\rangle)/\sqrt{1 + \eta^2},$$
$$|X'\rangle = (\eta|X_c\rangle - 1|X_a\rangle)/\sqrt{1 + \eta^2}, \qquad (13)$$

where $|X_c\rangle$ is a $\mathbf{k} = \mathbf{0}$ Bloch sum of cation p_x orbitals, $|X_a\rangle$ is the same quantity for anions, and η is the probability amplitude of the anion relative to the cation in the valence state. This quantity is given by $\eta = -(E_p^c - E_p^a + E_{g4})/2V_{xx}$ [29], in which E_p is the Hartree-Fock energy [27] of a valence atomic p state, $E_{g4} = [(E_p^c - E_p^a)^2 + 4V_{xx}^2]^{1/2}$, and $V_{xx} = 1.28\hbar^2/md^2$ [27], where d is the distance between neighboring atoms. Equation (13) may be used to evaluate the relevant spin-orbit parameters [17]:

$$\Delta_0 = (\Delta_c + \eta^2\Delta_a)/(1 + \eta^2),$$
$$\Delta_0' = (\eta^2\Delta_c + \Delta_a)/(1 + \eta^2), \qquad (14)$$
$$\Delta^- = \eta(\Delta_a - \Delta_c)/(1 + \eta^2),$$

in which Δ_c and Δ_a are the atomic spin-orbit splittings [28]. To complete the calculation of C_4, one may estimate Q from the measured Luttinger parameters γ_1 and γ_2 as follows [17]: $Q^2 = \hbar^2(\gamma_1 - 2\gamma_2 + 1)(E_0' + \tfrac{2}{3}\Delta_0')/2m$.

The results of these calculations are presented in Table I for several III-V semiconductors. The only input parameters were the lattice constant a ($d = \sqrt{3}\,a/4$) and the Luttinger parameters γ_1 and γ_2. In many cases the values of Δ_0, Δ_0', and E_{g4} ($E_{g4} = E_0' + \tfrac{1}{3}\Delta_0 + \tfrac{2}{3}\Delta_0'$) are known from experiment, so a comparison offers a good test for the reliability of the predicted values of Δ^-. Such a comparison is given for GaAs, InP, GaSb, and InSb, along with calculated values of Δ^- taken from Ref. [17]. The latter values were obtained from *ab initio* linear-muffin-tin-orbital calculations, which should be more accurate than Eq. (14). Experimental data for Δ^- from Ref. [26] are also included.

The agreement between calculated and experimental values of E_{g4}, Δ_0, and Δ_0' is quite good, given the simplicity of the model. In addition, the values obtained for Δ^- are similar to those of Refs. [17] and [26]—with the exception of InP, which has the right sign but is a factor of 2 to 4 too small. Hence, the tight-binding predictions for C_4 should be roughly correct, although they tend to be smaller than values obtained by other methods.

The results in Table I show that, as expected, C_4 is about an order of magnitude larger than C. The only significant exception occurs for InAs, where the unusually small value of C_4 (for such heavy atoms) is due to the similarity of the spin-orbit splittings of In and As.

The change in C_4 across a heterojunction could be as large as 0.48 eV Å if lattice matching were not an issue, but for nearly lattice-matched materials this change is considerably smaller. For example, at a GaAs/AlAs junction $\Delta C_4 = 0.02$–0.03 eV Å. In comparison, the X-Y valence-band mixing coefficient for GaAs/AlAs junctions was estimated to be 0.1–0.3 eV Å from a simple pseudopotential model [5], 0.4–0.5 eV Å from tight-binding calculations [11], and 0.6 eV Å from experimental data fitting [11]. Thus, the contribution from linear-$\mathbf{k}$ valence-band mixing is not likely to be significant in GaAs/AlAs, primarily because the atoms that differ (Ga and Al) are light atoms with small spin-orbit splitting. (Recently, however, Magri and Zunger [30] have asserted that the value of 0.6 eV Å obtained in Ref. [11] is at least an order of magnitude too large. If this is true, then the linear-$\mathbf{k}$ contribution would be significant.)

The situation is more favorable in the case of In$_{0.53}$Ga$_{0.47}$As/InP, where $\Delta C_4 = 0.14$–0.22 eV Å. Tight-binding calculations show that the X-Y mixing coefficient is about 2.9 eV Å for InAs-type interfaces and about 0.87 eV Å for InGaP-type interfaces [7]. Since ΔC_4 is

TABLE I. Estimated values for C_4 (eV Å) compared with data for C (eV Å) given in Ref. [16]. Input parameters are a (Å), γ_1, and γ_2, and the values generated by the model are E_{g4} (eV), Δ_0 (eV), Δ_0' (eV), Δ^- (eV), and Q (eV Å). Additional rows contain data from Refs. [17] and [26] for comparison.

Material	a	γ_1	γ_2	E_{g4}	Δ_0	Δ_0'	Δ^-	Q	C_4	C[a]
GaP	5.451	4.20	0.98	5.219	0.081	0.160	+0.036	8.01	+0.02	−0.0055
							+0.066[b]		+0.03	
AlP	5.464	3.34	0.70	5.178	0.061	0.030	−0.014	7.60	−0.01	
GaAs	5.653	7.10	2.02	4.643	0.386	0.209	−0.087	8.36	−0.05	−0.0036
				4.715[c]	0.340[c]	0.171[c]	−0.085[d]		−0.05	
							−0.069[b]		−0.04	
AlAs	5.660	3.45	0.68	4.609	0.363	0.082	−0.140	7.27	−0.07	−0.0020
InP	5.869	5.05	1.6	5.149	0.098	0.361	+0.095	7.46	+0.05	−0.0144
				4.969[c]	0.108[c]	0.50[c]	+0.22[d]		+0.11	
							+0.398[b]		+0.19	
InGaAs[e]	5.869	11.01	4.18	4.600	0.405	0.306	−0.043	7.88	−0.03	
InAs	6.058	20.4	8.3	4.590	0.418	0.395	−0.009	9.03	−0.01	−0.0112
GaSb	6.096	13.2	4.4	3.733	0.838	0.309	−0.300	8.43	−0.23	+0.0007
				3.77[c]	0.75[c]	0.33[c]	−0.28[d]		−0.21	
AlSb	6.136	5.55	1.29	3.680	0.812	0.185	−0.356	7.18	−0.23	−0.0060
							−0.448[b]		−0.29	
InSb	6.479	40.1	18.1	3.717	0.899	0.466	−0.194	7.99	−0.14	−0.0092
				3.918[c]	0.803[c]	0.39[c]	−0.244[d]		−0.17	

[a]Calculated value from Ref. [16].
[b]Value extracted from experimental data fitting in Ref. [26].
[c]Experimental data from Ref. [17].
[d]Calculated value from Ref. [17].
[e]This calculation was based on the virtual-crystal approximation.

16%–25% of the latter, linear-**k** mixing should have a measurable influence on optical anisotropy in this system. Like any spin-orbit-related effect, its magnitude is smaller than the corresponding spin-independent effects, but its influence should still be detectable.

In conclusion, it has been shown that the contribution from p-like Γ_4 states to the linear-**k** mixing of Γ_8 valence states is nonzero at a heterojunction and that its value is about an order of magnitude larger than the linear-**k** terms in a bulk crystal. This enhancement is sufficiently large to have measurable consequences for the optical anisotropy in the quantum-well Pockels effect.

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