

# Successes and failures of the $\mathbf{k}\cdot\mathbf{p}$ method: A direct assessment for GaAs/AlAs quantum structures

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The  $\mathbf{k}\cdot\mathbf{p}$  method combined with the envelope-function approximation is the tool most commonly used to predict electronic properties of semiconductor quantum wells and superlattices. We test this approach by comparing band energies, dispersion, and wave functions for GaAs/AlAs superlattices and quantum wells as computed directly from a pseudopotential band structure and using eight-band  $\mathbf{k}\cdot\mathbf{p}$ . To assure equivalent inputs, all parameters needed for the  $\mathbf{k}\cdot\mathbf{p}$  treatment are extracted from calculated bulk GaAs and AlAs pseudopotential band structures. Except for large exchange splittings in the in-plane dispersion for thin superlattices, present in pseudopotential calculations but absent from the  $\mathbf{k}\cdot\mathbf{p}$  results, we find generally good agreement for heterostructure hole bands within  $\pm 200$  meV of the GaAs valence-band maximum. There are systematic errors in band energies and dispersion for deeper hole bands

standard model, compromise its description of an  $A/B$  heterostructure. The fact that its parameters are usually fit to experimental data has also made it difficult to appraise these limitations. In contrast to the direct approach of Eqs. 1–4, the standard model (a) omits discrete crystal symmetries, e.g., point-group symmetry differences between an odd and even number of layers in  $A_nB_m$  superlattices<sup>11</sup> or thin films;<sup>12</sup> (b) usually assumes a constant potential in each region and neglects the spatial dependence of wave functions transverse to the heterostructure modulation direction; (c) attempts to describe nanostructure wave functions in terms of a few Bloch states, neglecting their differences in materials  $A$  and  $B$ ; and (d) can describe band dispersion only in an unspecified region near the heterostructure zone center.

Other methods have been applied to heterostructures, e.g., the tight-binding approach.<sup>13</sup> Although it preserves an atomistic description, like the  $\mathbf{k}\cdot\mathbf{p}$  approach it suffers from a

der flat band conditions, the  $A$  and  $B$  regions are assumed bulklike, and the wave function, e.g., in material  $A$ , takes the form

$$\psi(\mathbf{r}) = \sum_{n=1}^N F_n^A(\mathbf{r}) u_{nG}^A(\mathbf{r}), \quad (9)$$

where the  $F_n^A(\mathbf{r})$  are envelope functions and the zone-center states  $u_{nG}^A(\mathbf{r})$  are formally different in materials  $A$  and  $B$ . The sum runs over the  $N$  states retained in the  $\mathbf{k} \cdot \mathbf{p}$  description, defining a multiband EFA. By construction,<sup>15,24</sup> the  $F_n$  have Fourier components restricted to the first Brillouin zone of the  $A$  or  $B$  constituents and are thus fairly *slowly varying*.

eight zone-center states  $u_{n\mathbf{G}}(\mathbf{r})$ , in principle, differ in GaAs and AlAs. These differences are retained insofar as they enter matrix elements and affect, via material parameters, boundary conditions at interfaces between the two materials,<sup>25</sup> but are not included otherwise. The Kane parameter<sup>8</sup>  $B\delta$ , identically zero for systems with inversion symmetry, is assumed zero. The envelope function for band  $n$  is expanded for *both*  $A$  and  $B$  regions in supercell reciprocal lattice vectors appropriate to rectangular geometry:

$$F_n(\mathbf{r}) = \sum_{jlm}^{N_x N_y N_z} F_{jlm}^{(n)} \frac{1}{\sqrt{L_x L_y L_z}} \exp\{2\pi i[-jx/L_x - ly/L_y - mz/L_z]\}, \quad (11)$$

relying on Fourier representability to include the jump discontinuities in material properties at  $A/B$  interfaces. The boundary conditions applied to Eqs. (9) and (10) are discussed in detail in Refs. 22 and 25. Since the  $F_n$  are in general complex, both oscillatory and decaying contributions to each envelope function are naturally included, circumventing the need to explicitly include both.<sup>29</sup> For all of the geometries we consider, the system is uniform transverse to the superlattice or quantum well stacking direction, so the dimensions  $L_x$  and  $L_y$  are irrelevant and convergence is determined only by the number of Fourier components  $N_z$  retained. For specified  $\mathbf{k}$ , superlattice band energies and envelope functions are found from eigenvalues and eigenvectors of an  $8N_z$  square matrix. We have used  $N_z = 75$ ; even for the extreme short-period AlAs<sub>1</sub>-GaAs<sub>1</sub> superlattice, eigenvalues change by less than 0.2 meV on reducing  $N_z$  to 25.

#### IV. COMPARISONS OF “STANDARD MODEL” AND DIRECT CALCULATIONS

AlAs <sub>$n$</sub> -GaAs <sub>$n$</sub>  superlattices and GaAs <sub>$n$</sub> /AlAs quantum wells are conveniently described as tetragonal primitive cells. The Brillouin zone is shown in Fig. 1, where we use an overbar to indicate heterostructure states. We specify band energies for *bulk* zinc-blende AlAs and GaAs using conventional double group, i.e., relativistic, notation, but label heterostructure states via the zinc-blende Brillouin zone point from which they derive. The state  $\bar{G}(X_2)$ , for instance, is an  $\bar{001}$  heterostructure state at the tetragonal zone center  $\bar{G}$  derived from a zinc-blende  $X$  point state, which folds to  $\bar{G}$  due to the longer  $\bar{001}$  repeat distance. An arbitrary wave vector  $\mathbf{q}$  in the tetragonal zone can be resolved into components  $\mathbf{q}_\parallel$  along the stacking direction and an “in-plane” component  $\mathbf{q}_\perp$  perpendicular to it. The zinc-blende  $L$  point folds<sup>30</sup> to the tetragonal  $\bar{X}$  point for even  $n$  and to  $\bar{R}$  for odd  $n$ , while the tetragonal

ject. In particular, (a) since zinc-blende GaAs and AlAs are correctly described throughout the zinc-blende Brillouin zone, heterostructure  $X$ -derived bands will also be correctly described; (b) band dispersion throughout the heterostructure Brillouin zone may be computed with the same accuracy as for a zinc-blende material, since we use a fixed plane wave cutoff; (c) all features of wave functions, with oscillations of all wavelengths permitted by Bloch’s theorem, are included; (d) for a specified wave vector  $\mathbf{q}$ , all bands—not simply those which are derived directly from the three valence band and one conduction-band state retained in the  $8 \times 8 \mathbf{k} \cdot \mathbf{p}$  description—may be examined. For these reasons, we refer to the direct calculations below as an “all band pseudopotential” or ABP approach.

#### C. The standard model: Computational details

We use an  $8 \times 8 \mathbf{k} \cdot \mathbf{p}$  EFA method described in detail by Baraff and Gershoni<sup>25</sup> and reviewed by Gershoni *et al.*,<sup>22</sup> but use Luttinger parameters fit to our *calculated* pseudopotential bulk bands for GaAs and AlAs; see the Appendix. Pseudopotential-derived Luttinger parameters and effective masses differ somewhat from accepted values,<sup>22,27,28</sup> although the range of the latter may be large.<sup>28</sup> Our purpose is to compare in detail predictions of two *theoretical* approaches, using precisely equivalent inputs, not to exactly reproduce experimental data.

In the formalism of Baraff and Gershoni,<sup>25</sup> the wave function of the heterostructure is of the form in Eq. (9), where the

lations (solid lines) and within the eight-band  $\mathbf{k}\cdot\mathbf{p}$  approach (dashed), using pseudopotential-determined Luttinger parameters. On this scale,  $\mathbf{k}\cdot\mathbf{p}$  results appear parabolic; for GaAs, they agree with the correct dispersion of ABP bands to within 50 meV only up to 12%, 18%, 14%, and 14% of the distance toward  $X$  for the electron, heavy-hole, light-hole, and split-off bands, respectively; yet larger discrepancies occur farther from  $\Gamma$ . In particular, the GaAs  $\mathbf{k}\cdot\mathbf{p}$   $X_{6c}$  state is 26 eV higher than the correct ABP value, so that any  $\Gamma_{6c} \otimes X_{6c}$  coupling is unphysically negligible in  $\mathbf{k}\cdot\mathbf{p}$ .

### B. ABP electronic structure of $(\text{AlAs})_n(\text{GaAs})_n[001]$ superlattices

We begin by establishing overall trends with  $n$  for  $\Gamma_{6c}$  conduction-band states, using pseudopotential results (Fig. 3). We note the following.

(i) At the  $(\text{AlAs})_n(\text{GaAs})_n$  superlattice zone center,  $\bar{\Gamma}(\Gamma_{6c})$  states derive mostly from the zinc-blende GaAs conduction-band minimum  $\Gamma_{6c}$  state, while  $\bar{\Gamma}(X_z)$  states derive mostly<sup>30</sup> from the zinc-blende first  $X_{6c,z}$  and second  $X_{7c,z}$  conduction states at  $X$ . For even (odd)  $n$

parisons with envelope functions. We note that -a! for  $n \leq 7$  both electrons and holes are localized primarily within the GaAs region, while for  $n \leq 6$  electrons are found with comparable probabilities in both regions. For  $n \geq 6$  -not shown! the CBM is more strongly localized in the AIAs region, while the VBM remains GaAs-like, confirming that this band crossing marks a transition for the GaAs/AIAs system from a type II -electrons and holes localized in different spatial regions! to a type I superlattice -electrons and holes localized in the same spatial region!. Also, -b! the CBM shows prominent peaks<sup>34</sup> -indicated by asterisks! near GaAs/AIAs interfaces.

-iii! The nonfolding  $\bar{M}(X_{x,y})$  states shown in Fig. 3 are relatively insensitive to  $n$  and slowly approach the bulk AIAs  $X_{6c}$  state for very large  $n$ .

-iv! The zinc-blende  $L$ -derived points  $\bar{R}(L)$  -for odd  $n$  and  $\bar{X}(L)$  -for even  $n$  oscillate<sup>30</sup> strongly for small  $n$  and asymptotically approach the GaAs  $L_{6c}$  conduction-band minimum for large  $n$ .

-v! The  $n \leq 1$  superlattice is indirect via the  $\bar{R}$  point, while the  $n \leq 2, 3, 4,$  and  $6$  superlattices are pseudodirect via the  $\bar{G}(X_z)$  point, coupled to the VBM by weak dipole matrix elements typical of folded-in states. Curiously, for  $n \leq 5$ , the  $\bar{Z}$  point, 2.3 meV below  $\bar{G}(X_z)$ , is the conduction-band minimum.

Effects -i! -v! are *all absent from the "standard model."* In particular, the nonmonotonic dependence of band energies on  $n$  -i! and -iv! above# is mandated in the pseudopotential approach by changes in point group symmetries<sup>11</sup> with  $n$ . Input parameters to the two classes of calculations emphasize profound physical differences in the symmetries retained: The ABP approach requires specification of microscopic atomistic quantities, i.e., primitive translation vectors for the structure, the identity and coordinates of all atoms within the primitive cell, and pseudopotentials for all distinct atom types. Standard model calculations require only the heterostructure orientation and *continuum*

## *2. Near-edge wave functions at $\bar{G}$*

Is the good agreement between the pseudopotential and the standard model approaches for near-edge hole states, but poor agreement for the  $\bar{G}(G_6)$

tion. In contrasting ABP and the SM, we note that -i! the spin splitting is nonzero and significant in the ABP results for valence bands;<sup>35</sup> -ii! apart from the shift discussed earlier, once again, dispersion of the  $\bar{G}(G_{6c})$  electron band is well described for  $q_{\perp}a/2\rho \approx 0.05$ ; -iii! despite an underestimate of the band energy which increases with  $q_{\perp}$ , the SM reproduces a shallow minimum of the  $s-o1$  band at  $q_{\perp}a/2\rho \approx 0.08$ ; -iv! even for  $n \leq 5$ , band dispersion is quite anisotropic. The ABP values for  $m_{\parallel}/m_{\perp}$  at  $\bar{G}$



slight increase -with respect to that for the superlattice geometry! in the number of monolayers required for the type II to type I transition for the quantum well geometry has been noted by Mäder, who used an empirical tight-binding Green's function approach;<sup>36</sup> -iii! the energy of the  $\bar{G}(G_{6c}$

until GaAs thicknesses of  $\sim 40 \text{ \AA}$ . For *valence* states, -i! the SM is generally good for hh1 and lh1 bands, but deteriorates deeper into the valence band and away from the zone center  $\bar{G}$ ; -ii! neglects spin splittings when the spin degeneracy is lifted, e.g., for in-plane dispersion. With respect to the ABP, the standard model overestimates electron and hh1 effective masses  $m_i$  for dispersion along  $\Gamma\text{-}001$  and underestimates the effective

### **B. Analysis of ABP results via projections**

Because near-edge GaAs/AIAs heterostructure states are often derived largely from GaAs bands, for convenience we project on zinc-blende GaAs states. Due to the great similarity of GaAs and AIAs, results would be very similar had AIAs Bloch states been used. We emphasize that a large projection onto GaAs for a superlattice state need *not* imply

projections. If so, why is the standard model unsatisfactory for superlattice conduction and deep hole bands? Figure 2 and the projections in Table II permit a reassessment of the  $\mathbf{k} \cdot \mathbf{p}$  EFA errors noted above. We will show that most errors may be traced simply to a poor  $\mathbf{k}$

*served* only<sup>44</sup> at finite values of the in-plane wave vector  $\mathbf{q}_\perp$ , where it is attributed<sup>44</sup> to nonparabolicities of the zinc-blende valence bands. Using an empirical pseudopotential approach, Edwards and Inkson<sup>45</sup> have examined hole states in GaAs/AlAs double barrier and multiple quantum well structures. They find pairs of lh-hh resonances in the transmission coefficient which they trace to the *differences* in the cell-periodic functions  $u_{n\mathbf{G}}(\mathbf{r})$  in GaAs and AlAs (see Eq. 9). They note that the behavior they find for finite  $\mathbf{q}_\perp$  is qualitatively similar to that at  $\bar{G}$ , suggesting that mixing is important there. For our calculations at  $\bar{G}$ , which fully retain such differences in the GaAs/AlAs  $u_{n\mathbf{G}}(\mathbf{r})$ , such mixing is extremely small for the hh1 and lh1 states, although the mixed character of deeper valence bands increases.

### 3. Analysis of standard model errors via projections

The previous section implies that *provided* the dispersion of each bulk band is properly described, as is the case for the pseudopotential GaAs band structure of Fig. 2, a relatively small number of near-edge zinc-blende bands is sufficient to quantitatively describe the heterostructures above in terms of

ductors. From such calculations for GaAs and AlAs we extracted the Luttinger parameters required for an 8-band  $\mathbf{k} \cdot \mathbf{p}$  EFA description of  $(\text{AlAs})_n(\text{GaAs})_n$  superlattices and  $(\text{GaAs})_n$

simply from the  $DE$  at the first grid point, since no terms linear in  $Dk$  were observed in our fits.

To compute band energies for heterostructures, we require one additional parameter, which is *not* a property of a pure material in isolation. This is the valence-band offset  $(DV)_{\text{VBM}}$  between the two materials -Table IV!. The process of generating the pseudopotentials used in our calculations<sup>2</sup> naturally includes the *experimental* value for the valence-band offset. Table IV gives band parameters for GaAs and AlAs and the Luttinger parameters extracted by solving the first five of Eqs. -A1!. Columns labeled<sup>22,27</sup> Gershoni, Henry, and Baraff -GHB! and Ram-Mohan, Yoo, and Aggarwal -RYA! give an indication of the variation in parameters used in  $\mathbf{k}\cdot\mathbf{p}$  EFA calculations, although band effective masses, for example, are relatively insensitive<sup>48</sup> to Luttinger parameters. From our calculated values, we can examine some aspects of the consistency of the Luttinger description of bulk bands. In the  $\langle 111 \rangle$  direction, for example, the light- and

heavy-hole effective masses depend @Eq. -A1!# only on the Luttinger parameters  $g_1$  and  $g_3$ , both of which are known from fitting five of the six equations above to the six -calculated! band effective masses. We will, for convenience, regard the equation for  $m_{\text{lh}\langle 111 \rangle}/m_0$  as a check on the presumed values of  $g_1$  and  $g_3$ . We thus have an error in the  $\langle 111 \rangle$  light-hole effective mass of

$$\frac{Dm_{\text{lh}}}{m_{\text{lh}}^{\text{ABP}}} \approx \begin{cases} 22.1\%, & \text{GaAs} \\ 1.016\%, & \text{AlAs.} \end{cases}$$

Thus the assumptions made in the Kane model parametrization for bulk GaAs and AlAs are quite well obeyed by

- tron. Electron Phys. **72**, 1 -1988!
- <sup>11</sup>K. Ebertl, W. Wegscheider, and G. Abstreiter, Superlatt. Microstruct. **9**, 31 -1991!
- <sup>12</sup>S. B. Zhang, C.-Y. Yeh, and A. Zunger, Phys. Rev. B **48**, 11 204 -1993!
- <sup>13</sup>D. L. Smith and C. Mailhot, Rev. Mod. Phys. **62**, 173 -1990!, review tight-binding descriptions of semiconductor heterostructures. Section IV compares predictions of  $\mathbf{k}\cdot\mathbf{p}$  EFA with other theoretical methods.
- <sup>14</sup>L. J. Sham and Y.-T. Lu, J. Lumin. **44**, 207 -1989!
- <sup>15</sup>J. M. Luttinger and W. Kohn, Phys. Rev. **97**, 869 -1955!
- <sup>16</sup>For a specified Hamiltonian, degenerate perturbation theory -DPT! differs from full diagonalization only in how the set of basis functions is chosen. In DPT *only* basis functions strongly coupled by the perturbation are retained; a complete set is not used. When the perturbation is strong enough to couple significantly to states *outside* the set, DPT fails or, in the general case, basis set incompleteness effects begin.
- <sup>17</sup>States not explicitly included in the truncated set of zone-center states could be included by Löwdin perturbation theory. See the reviews of Kane -Refs. 7 and 8!; C. Priester and M. Lannoo, Phys. Rev. B **44**, 10 559 -1991! discuss the effect of Löwdin perturbation theory on band nonparabolicity. The conventional Kane model -Refs. 7 and 8! includes parameters that for cubic systems acquire nonzero values *only* through couplings to states outside the set retained. Elements of the matrix in Eq. -7! are thus formally energy-dependent perturbation sums of momentum matrix elements. In practice, the fitting process circumvents this procedure, however.
- <sup>18</sup>L.-W. Wang and A. Zunger -unpublished!
- <sup>19</sup>P. P. von Allmen, Phys. Rev. B **46**, 15 382 -1992!
- <sup>20</sup>A. T. Meney, B. Gonul, and E. P. O'Reilly, Phys. Rev. B **50**, 10 893 -