Million-Atom Pseudopotential Calculation of Γ-*X* Mixing in GaAs/AlAs Superlattices and Quantum Dots

Lin-Wang Wang, Alberto Franceschetti, and Alex Zunger
National Renewable Energy Laboratory, Golden, Colorado 80401
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We have developed a "linear combination of bulk bands" method that permits atomistic, pseudopotential electronic structure calculations for $> 10^6$ atom nanostructures. Application to $(\mathrm{GaAs})_n/(\mathrm{AlAs})_n$ (001) superlattices (SL's) reveals even-odd oscillations in the G-*X* coupling magnitude $V_{GX}(n)$, which vanishes for *n* - odd, even for *abrupt* and *segregated* SL's, respectively. Surprisingly, in contrast with recent expectations, 0D quantum dots are found here to have a *smaller* G-*X* coupling than equivalent 2D SL's. Our analysis shows that for large quantum dots this is largely due to the existence of level repulsion from *many X* states. [S0031-9007(97)02839-1]

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The crossover from direct band gap to indirect band gap (e.g., $\Gamma \rightarrow X$) as a function of an external parameter is common in semiconductor physics. It is seen in (i) zinc blende materials (GaAs [1], InP [2]) as a function of pressure, (ii) alloys ($Al_xGa_{1-x}As$ [3], $Ga_xIn_{1-x}P$ [4]) as a function of composition *x*, and (iii) in superlattices (SL's) [5–9] and quantum dots [10,11] as a function of size or external pressure. While in cases (i) and (ii) the transition is believed to be first order [3], in nanostructures [case (iii)] the lack of translational invariances causes a quantum-mechanical mixing between the zone center Γ and the zone edge *X* states [12], measured by the coupling matrix element V_{GX}. Although small in magnitude (V_{GX} , 10 meV), the G-*X* coupling has profound consequences on the properties of the system, leading, for example, to the appearance of indirect transitions without phonon intervention [7,8], to characteristic pressure-induced changes of the photoluminescence intensity [9,10], to resonant tunneling in electronic transmission between GaAs quantum wells separated by an AlAs barrier [13] and to level splitting ("avoided crossing") in the pressure, electric-field, and magnetic-field induced G-*X* transition [5,6].

The significance of this small but crucial quantum-mechanical coupling has prompted attempts to measure $V_{GX}(m, n)$ in $(\mathrm{GaAs})_m/(\mathrm{AlAs})_n$ (001) superlattices, producing, however, widely scattered results: Meynadier *et al.* [5] found from the electric-field dependence of the photoluminescence energy $V_{GX}(12, 28)$ - 1.25 meV, while Pulsford *et al.* [6] found from the magnetic-field induced gap in the Landau level $V_{GX}(9, 3)$ - 9 meV. Measurements of the valence (v) to conduction (*c*) $\Gamma_v \leftrightarrow \Gamma_c$ and $\Gamma_v \leftrightarrow X_c$ emission [7] or absorption [8] fitted to theoretical models produced $V_{GX}(10, 10)$ - 1.2 meV in Ref. [7] and $V_{GX}(4, 10)$ - 0.99 meV in Ref. [8].

The calculation of V_{GX} is difficult, as highlighted by the fact that the central approximation underlying the "standard model" of nanostructure physics–the conventional $\mathbf{k} \cdot \mathbf{p}$ model [14]—leads to V_{GX} - 0. Tight-binding

($\mathbf{k} = 0$) bulk Bloch functions $|u_{n,0}\rangle$ are used to construct the basis functions $f_a(\mathbf{r}) = u_{n,0}(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}}$. The wave function of the nanostructure is then expanded as

$$\psi_i(\mathbf{r}) = \sum_{n,\mathbf{k}} C_{n,\mathbf{k}}^{(i)} \{u_{n,0}(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}}\}. \quad (2)$$

The disadvantage of this approach is that it is unable to reproduce the band structure across the Brillouin zone; in particular, the bulk X_{1c} state is misplaced by $.10$ eV, as recently shown by Wood *et al.* [23,24], with the consequence that $V_{GX} \neq 0$ for all nanostructures.

The solution to this dilemma is to replace the zone-center states $|u_{n,0}\rangle$ in Eq. (2) with the bulk Bloch states $|u_{n,\mathbf{k}}\rangle$, leading to the linear combination of bulk bands method. For a periodic system consisting of materials A and B, Eq. (2) becomes

$$\psi_i(\mathbf{r}) = \sum_{s=A,B} \sum_{n,\mathbf{k}}^{N_b, N_\mathbf{k}} C_{n,\mathbf{k},\sigma}^{(i)} \{u_{n,\mathbf{k}}^{s}(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}}\}, \quad (3)$$

where the first sum runs over the constituent materials A and B, and the second sum runs over the bulk band index n and the supercell reciprocal lattice vectors $\mathbf{k}$ belonging to the first Brillouin zone of the underlying lattice. The advantage of the LCBB method over the conventional $\mathbf{k}\cdot\mathbf{p}$ method is that off-G states $u_{n,\mathbf{k}\neq\mathbf{0}}^{s}$ of both materials can be directly included in the basis set, thus eliminating the need for hundreds of $\mathbf{k}$ -

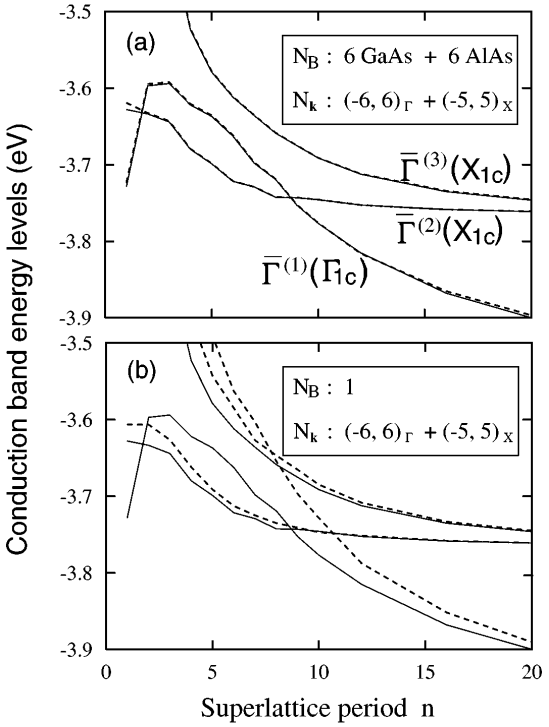

FIG. 1. Energy of the three lowest conduction states at the G point of (001) $(GaAs)_n(AlAs)_n$ superlattices, obtained using different truncations (insets) in the number of bands N_B and the number of **k** points $N_{\mathbf{k}}$ in Eq. (3).

distance between the G and X curves, is 0.9 meV for $n = 20$. This value should be compared with 1.2 meV we obtained from an exact calculation (i.e., no truncation in N_B or $N_{\mathbf{k}}$). Figure 2(c) shows the VBM → CBM (conduction-band minimum) momentum transition matrix element $|\langle c_{\mathrm{VBM}}|\mathbf{p}|c_{\mathrm{CBM}}\rangle|^2$ as a function of pressure. We see that unlike alloys [3], the transition in superlattices (and dots) is *not* first order. The finite G-X coupling V_{GX} leads to the presence of some G character even in the "indirect gap region" ($P > P_c$), producing there *a finite optical transition probability*.

In the above calculations we assumed ideal, sharp interfaces. To see whether interfacial roughness, present in real samples, can quench the G-X coupling, we have compared V_{GX} for $(GaAs)_n(AlAs)_n$ superlattices with sharp interfaces and with realistic segregated profiles obtained by solving the segregation equation [27]. The results (Fig. 3) show that while segregation reduces V_{GX} by about a factor of 2, the odd-even oscillations of V_{GX} with the period n are not washed out. In fact, while for *abrupt* SL's [Fig. 3(a)], $V_{GX} = 0$ for n - odd, in segregated SL's, $V_{GX} \neq 0$ for n - even [Fig. 3(b)]. Our calculated $V_{GX} = 1.24$ meV for a sharp $(GaAs)_{12}(AlAs)_{28}$ SL, is in excellent agreement with the experimental [5] value of 1.25 meV.

We next study G-X coupling in GaAs dots embedded in AlAs matrix. To compare meaningfully the G-X coupling in quantum dots and superlattices, we have chosen a particular dot geometry (inset of Fig. 4): 20 monolayers (ML) of GaAs sandwiched by 20 ML of AlAs in the [001] direction and N ML of GaAs surrounded by 20 ML of AlAs in the [110] and {110} directions. Thus, when $N \to \infty$ the quantum dot merges into a 20 × 20 [001] superlattice. The pressure dependence of the transition energies and of the momentum matrix element for a $N = 140$ quantum dot are shown in Figs. 2(b) and 2(c) (where the supercell contains 2×10^6 atoms). The calculation takes ≈ 30 min on a IBM RS6000 work station model 590 for one pressure value. We find that the G-X coupling in these QD's is *smaller* than in the corresponding 20 × 20 superlattice [compare Fig. 2(a)]. Furthermore, as shown in Fig. 4, the anticrossing gap $\Delta E_{\min}$ ($= 2V_{GX}$ in two level systems) in dots does not approach the superlattice value when N increases. There are two reasons for this: (i) For small dots, the 20 ML barrier region of AlAs in [110] and

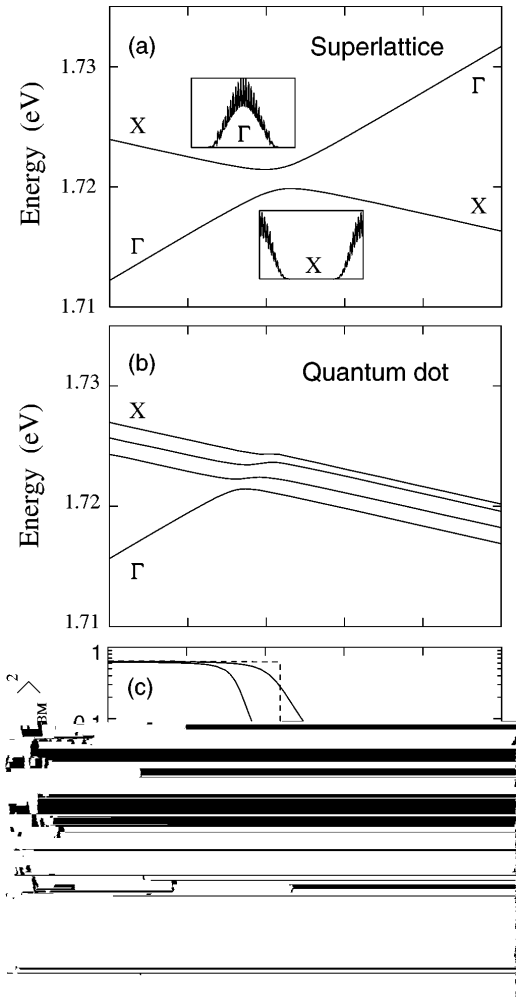

FIG. 2. Pressure dependence of the transition energies from the VBM to the G and X-derived conduction bands (a) and (b) and transition probabilities (c) of a $(GaAs)_{20}(AlAs)_{20}$ superlattice and a 20 × 140 × 140 quantum dot. The insets in part (a) show the G and X wave functions along the [001] direction of the superlattice. The dashed line in part (c) gives the SL transition probability expected in the absence of G-X coupling.

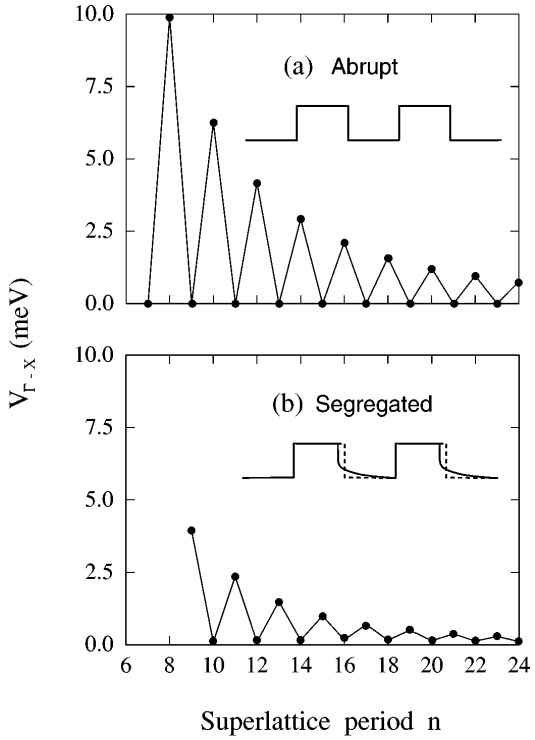
10.0
7.5
5.0
2.5
0.0
(a) Abrupt
10.0
7.5
5.0
2.5
0.0
(b) Segregated
$V_{\Gamma-X}$ (meV)
6 8 10 12 14 16 18 20 22 24
Superlattice period n

FIG. 3. G-*X*