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

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We have developed a "linear combination of bulk bands" method that permits atomistic, pseudopotential electronic structure calculations for $\sim 10^6$ atom nanostructures. Application to $(\mathrm{GaAs})_n/(\mathrm{AlAs})_n$ (001) superlattices (SL's) reveals even-odd oscillations in the Γ-X coupling magnitude $V_{\Gamma X}(n)$, 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* Γ-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 ($\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ [3], $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}$ [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 $V_{\Gamma X}$. Although small in magnitude ($V_{\Gamma X} \sim 10$ meV), the Γ-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 Γ-X transition [5,6].

The significance of this small but crucial quantum-mechanical coupling has prompted attempts to measure $V_{\Gamma X}(m, n)$ 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 $V_{\Gamma X}(12, 28) = 1.25$ meV, while Pulsford *et al.* [6] found from the magnetic-field induced gap in the Landau level $V_{\Gamma X}(9, 3) = 9$ 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 $V_{\Gamma X}(10, 10) = 1.2$ meV in Ref. [7] and $V_{\Gamma X}(4, 10) = 0.99$ meV in Ref. [8].

The calculation of $V_{\Gamma X}$ 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 $V_{\Gamma X} = 0$. Tight-binding

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

$$\psi_i(\mathbf{r}) = \sum_{n,\mathbf{k}} C^{(i)}_{n,\mathbf{k}} \left[u_{n,0}(\mathbf{r})\, e^{i\mathbf{k}\cdot\mathbf{r}}\right]. \qquad (2)$$

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 $V_{\Gamma X} < 0$ 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

$$\psi_i(\mathbf{r}) = \sum_{\sigma = A,B} \sum_{n,\mathbf{k}}^{N_b, N_\mathbf{k}} C^{(i)}_{n,\mathbf{k},\sigma} \left[u^{\sigma}_{n,\mathbf{k}}(\mathbf{r})\, e^{i\mathbf{k}\cdot\mathbf{r}}\right], \qquad (3)$$

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-Γ states $u^{\sigma}_{n,\mathbf{k}\neq\mathbf{0}}$ of both materials can be directly included in the basis set, thus eliminating the need for hundreds of $\mathbf{k} =$

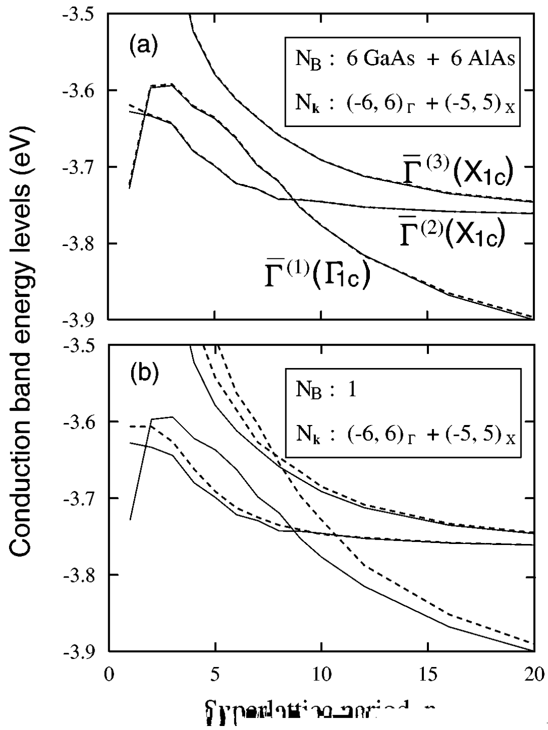

FIG. 1. Energy of the three lowest conduction states at the G point of (001) sGaAsd$_n$ysAlAsd$_n$ superlattices, obtained using different truncations (insets) in the number of bands N_B and the number of $\mathbf{k}$ points $N_\mathbf{k}$ in Eq. (3).

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 $V_{\mathrm{G}X}$ 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 $V_{\mathrm{G}X}$ for sGaAsd$_n$ysAlAsd$_n$ 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 $V_{\mathrm{G}X}$ by about a factor of 2, the odd-even oscillations of $V_{\mathrm{G}X}$ with the period n are not washed out. In fact, while for *abrupt* SL's [Fig. 3(a)], $V_{\mathrm{G}X}$ - 0 for n - odd, in segregated SL's, $V_{\mathrm{G}X}$ ø 0 for n - even [Fig. 3(b)]. Our calculated $V_{\mathrm{G}X}$ - 1.24 meV for a sharp sGaAsd$_{12}$ysAlAsd$_{28}$ 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 f1$\bar{1}$0g directions. Thus, when N → ‘ the quantum dot merges into a 20 3 20 [001] superlattice. The pressure dependence of the transition energies and of the momentum matrix element for a N - 140 quantum dot are shown in Figs. 2(b) and 2(c) (where the supercell contains 2 3 10^6 atoms). The calculation takes , 30 min on a IBM RSy6000 work station model 590 for one pressure value. We find that the G-X coupling in these QD's is *smaller* than in the corresponding 20 3 20 superlattice [compare Fig. 2(a)]. Furthermore, as shown in Fig. 4, the anticrossing gap DE_{min} (- 2$V_{\mathrm{G}X}$ 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

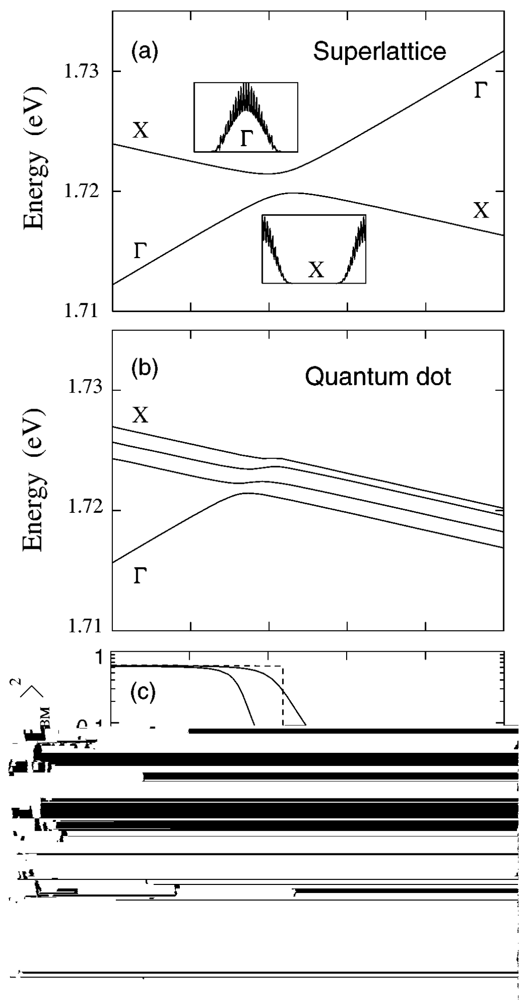

FIG. 2. Pressure dependence of the transition energies from the VBM to the G and X-derived conduction bands (a) and (b) and transition probabilities (c) of a sGaAsd$_{20}$ysAlAsd$_{20}$ superlattice and a 20 3 140 3 140 quantum dot. The insets in part (a) show the G and X wave functions along the [001] direction of the superlattice. The dashed line in part (c) gives the SL transition probability expected in the absence of G-X coupling.

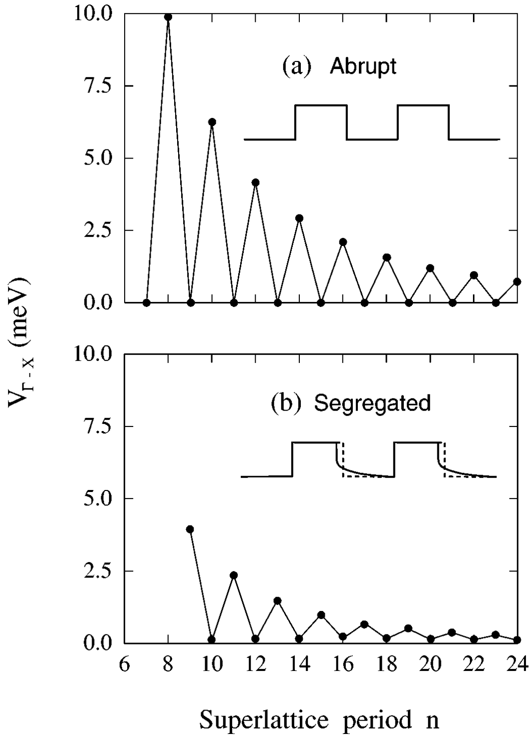
(a) Abrupt
(b) Segregated
$V_{\Gamma\text{-}X}$ (meV)
Superlattice period n
10.0
7.5
5.0
2.5
0.0
6
8
10
12
14
16
18
20
22
24

FIG. 3. G-*X*