

Effects of Γ - X mixing on the binding energy of a shallow donor in an AlAs/GaAs quantum well

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The effects of mixing between the Γ and X valleys of the conduction band on the binding energy of a shallow donor in a thin type-I AlAs/GaAs quantum well are investigated. The multivalley effective-mass equations are solved variationally, with a separable hydrogenlike trial function. The binding energy, as a function of well width, is found to be almost the same as in the zero-mixing case, except in the vicinity of the type-I-to-type II crossover, where mixing leads to a fundamentally different behavior, namely, instead of decreasing monotonically with increasing well width, the binding energy presents a peak close to the crossover. Using a renormalized effective mass for the Γ point in the AlAs layers, the interaction with the valence band is estimated to the first order and shown to be quite important.

GaAs/AlAs quantum wells and superlattices grown epitaxially are semiconductor heterostructures of special interest. They can be fabricated with excellent material quality and layer-thickness control. The band structure of both materials is very well known. AlAs is an indirect gap semiconductor with a triple degenerate conduction band minimum at the X point of the Brillouin zone,¹ while GaAs has a direct band gap at the zone center or Γ point. A mixing between the X valleys along the growth direction (assumed parallel to the [100] crystal axis) and the Γ valleys in both materials is expected to occur due to the break of translational symmetry in that direction. The effects of such mixing on the optical properties of short period superlattices²⁻⁷ or narrow quantum wells⁸ (QW's) and on the resonant tunneling through single and double barriers⁹⁻¹³ have been extensively studied. In the case of a superlattice, experiments have confirmed that the mixing causes the appearance of an anticrossing in the dispersion relation, where the pure Γ and pure X conducting minibands would cross if calculated independently, i.e., without coupling. This so-called Γ - X mixing should affect also the binding energy (E_B) of an electron bound to a shallow donor inside a GaAs/AlAs quantum well near the type I-to-type II crossover.⁸

Shallow impurities in GaAs/Ga_{1-x}Al_xAs quantum wells have been studied by several groups both theoretically¹⁴⁻²⁰ and experimentally.^{21,22} The theories are based on the effective mass approximation, but the effects of the X valleys which are below the Γ valley, when the concentration of aluminum is larger than 45%, have not been discussed. This is due to difficulties in including the Γ - X mixing into the effective mass approach and to the fact that the experiments probing these impurity states have not looked at narrow enough wells to see considerable effects from the mixing.^{21,22} More recent experiments have shown that the type I-to-type II crossover in a GaAs/AlAs quantum well occurs at a GaAs layer width, or quantum well width, ~ 35 Å.⁸ The crossover happens

when, by decreasing the well width, the bottom of the first subband matches the X conduction band edge in the AlAs layer. It is near this crossover that the effects of the Γ - X mixing on the binding energy of a shallow donor inside the well are expected to be most important. We show in this Rapid Communication that the binding energy of a donor in a type-I AlAs/GaAs quantum well, as a function of the well width L , presents a maximum just before the crossover. This maximum is due to the increasing leakage of probability into the AlAs layers through the X channel, which takes the electron away from the impurity, and thereby reduces the binding energy.

All theoretical calculations of the binding energy of impurities in quantum wells performed so far have represented just small ($\leq 10\%$) corrections to the pioneering infinite barrier calculation by Bastard,¹⁴ except for very narrow wells. More realistic models^{15,18} give an $E_B(L)$ curve with a maximum at small L and $E_B(L=0)$ equaling the bulk value for the barrier material, instead of the monotonic behavior obtained with the infinity barrier approximation, which leads to a $E_B(L=0) = 4 \text{ Ry}^*$, corresponding to the two-dimensional limit. The maximum we obtain is physically similar but has a nontrivial origin in the Γ - X interaction and occurs, in the case of a GaAs/AlAs quantum well, at a much larger value of L .

The potential added by the impurity turns the first-principles or semiempirical methods for electronic structure calculation helpless or at least computationally limited. Much effort has been dedicated to the extension of the effective mass approximation to treat the Γ - X mixing.^{3,10,23} The mixing occurs at the interface and should be incorporated through the boundary conditions for the envelope functions for both valleys and its derivatives. Three such boundary conditions have been suggested and shown to describe quite well the main features of the experiments.^{3,10,23} We perform here, within the effective mass approximation, a first variational calculation of the binding energy of a shallow donor located at the center of

an AlAs/GaAs quantum well including the Γ - X interaction.

We start with the multivalley effective mass approximation for a shallow impurity in bulk.^{24,25} The wave function is expanded in terms of the conduction band Bloch function (the effects of other bands are neglected) and it is assumed that the main contributions come from states around both minima, so that the wave function can be approximated by the sum of the Bloch functions from the Γ and X minima, modulated by slowly varying envelope functions,^{24,25} i.e.

$$\psi(\mathbf{r}) = \phi' \mathbf{F} = [\phi_{\Gamma}(\mathbf{r}) \phi_X(\mathbf{r})] \begin{bmatrix} F_{\Gamma}(\mathbf{r}) \\ F_X(\mathbf{r}) \end{bmatrix}, \quad (1)$$

where ϕ_{α} and F_{α} are the Bloch and envelope functions for the minimum α , respectively. Neglecting the valley mixing due to the rapidly varying potential around the core of the impurity,²⁶ the problem of the shallow donor in the bulk is described by the following uncoupled effective mass equations:

$$\begin{bmatrix} h_{\Gamma} & 0 \\ 0 & h_X \end{bmatrix} \begin{bmatrix} F_{\Gamma}(\mathbf{r}) \\ F_X(\mathbf{r}) \end{bmatrix} = \varepsilon \begin{bmatrix} F_{\Gamma}(\mathbf{r}) \\ F_X(\mathbf{r}) \end{bmatrix}, \quad (2)$$

with

$$h_{\alpha} = -\frac{\hbar^2}{2m_{\alpha\parallel}} \frac{\partial^2}{\partial z^2} - \frac{\hbar^2}{2m_{\alpha\perp}} \left(\frac{1}{\rho} \frac{\partial}{\partial \rho} + \frac{\partial^2}{\partial \rho^2} \right) + U(\mathbf{r}) + \varepsilon_{\alpha}, \quad \alpha = \Gamma, X, \quad (3)$$

where $\rho = (x^2 + y^2)^{1/2}$ and $r = (\rho^2 + z^2)^{1/2}$. The parallel and perpendicular indices refer to the growth (z) direction. ε_{α} is the conduction band edge at the point α in \mathbf{k} space. In the case of a QW, the effective masses $m_{\alpha\parallel}$ and $m_{\alpha\perp}$ depend on z and the band edges form a potential profile as shown in Fig. 1. We will make the simplification of using the same dielectric constant κ in both materials,²⁷ and use the unscreened Coulomb potential, $U(\mathbf{r}) = -e^2/\kappa r$.

For a complete mathematical description of the problem, we need to know the boundary conditions at the interface, which will incorporate the mixing. The connection formulas for the envelope functions and its derivatives can only be determined from first principles or semiempirical methods able to model the interface microscopic potential. Unfortunately, this is not an easy task. Ando and

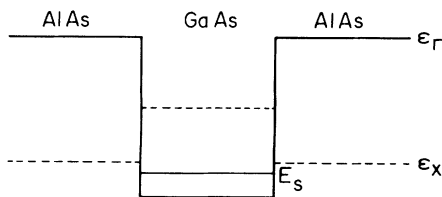


FIG. 1. Illustration showing the profile of a type-I AlAs/GaAs quantum well. The dashed line gives the variation of the energy of the X conduction band edge along the growth direction and the solid one gives that for the Γ valley. The bottom of the lowest conduction subband E_s is also assigned.

Akera²³ calculated approximate connection formulas using an sp^s* tight-binding model. Instead, we use here the much simpler phenomenological formula suggested by Pulsford *et al.*³ It is assumed that the Bloch functions on both sides of the interface are connected by a single parameter unitary matrix:

$$T = \begin{bmatrix} (1 - \gamma^2)^{1/2} & -\gamma \\ \gamma & (1 - \gamma^2)^{1/2} \end{bmatrix}, \quad (4)$$

where γ expresses the amount of mixing. Pulsford *et al.*³ obtained good agreement with experiment with $\gamma = 0.04$.

The requirement that the total wave function ψ must be continuous leads to the following condition for the envelope functions at the interface:

$$\mathbf{F}_1 = \mathbf{T} \mathbf{F}_2, \quad (5)$$

where 1 denotes GaAs ($|z| < l$) and 2 denotes AlAs ($|z| > l$). The well width is $L = 2l$.

The boundary conditions for the derivatives are obtained from the condition of current probability or flux conservation. Since \mathbf{T} is unitary, by using the probability current operator corresponding to the Hamiltonian in (2), one can show that we must have

$$\mathbf{M}_1^{-1} \frac{d}{dz} \mathbf{F}_1 = \mathbf{T} \mathbf{M}_2^{-1} \frac{d}{dz} \mathbf{F}_2, \quad (6)$$

where

$$\mathbf{M}^{-1} = \begin{bmatrix} 1/m_{\Gamma\parallel} & 0 \\ 0 & 1/m_{X\parallel} \end{bmatrix}. \quad (7)$$

In this work we also study the first-order correction due to the interaction with the valence band as given by a renormalized effective mass.²⁸ It has been pointed out that significant corrections to the one-band effective mass approximation derives from the large Γ band offset in AlAs/GaAs heterostructures (~ 1 eV). States with energy close to the bottom of the well in an AlAs/GaAs quantum well have energy almost as far from the AlAs Γ conduction band edge as from the GaAs valence band maximum. Following Brozak *et al.*²⁸ we made the calculations with both effective masses for the AlAs Γ states: the band edge one of $0.15m_e$ and the renormalized one of $0.09m_e$. As we are interested here in narrow wells (large energies), the corrections due to the next order term in the renormalized effective mass expansion are bigger than those in Ref. 28, but yet small, of the order of 7%, and were not considered.

The binding energy is the difference between the unperturbed subband edge (E_s) and the bound state energy (ε), i.e., $E_B = E_s - \varepsilon$. To find the subband edge, we set $U(\mathbf{r}) = 0$ and solve (2). The solution for the lowest conducting state in a type-I QW is

$$\mathbf{F}_s = \begin{cases} \mathbf{F}_{s1} = \begin{bmatrix} A_{\Gamma 1} \cos(k_{\Gamma 1} z) \\ A_{X 1} \cosh(k_{X 1} z) \end{bmatrix}, & 0 \leq z < l, \\ \mathbf{F}_{s2} = \begin{bmatrix} A_{\Gamma 2} e^{-k_{\Gamma 2} z} \\ A_{X 2} e^{-k_{X 2} z} \end{bmatrix}, & l > z, \end{cases} \quad (8)$$

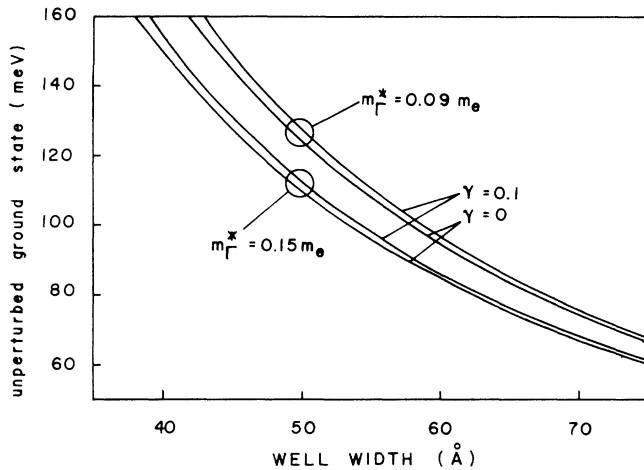


FIG. 2. Unperturbed subband edge E_s calculated with zero and 10% mixing ($\gamma=0$ and 0.1 , respectively). Results are shown for both, the band edge AlAs Γ effective mass of $0.15m_e$ and the renormalized one due to the interaction with the valence band, which is 35% smaller.

where the wave numbers (or decay rates) are given by

$$k_{ai} = \frac{(2m_{ai}|E_s - \epsilon_{ai}|)^{1/2}}{\hbar}, \quad \alpha = \Gamma, X, \quad i = 1, 2. \quad (9)$$

The boundary conditions (5) and (6) lead to four equations for the four constants A_{ai} , and from the characteristic equation we determine E_s .

Now we turn on the Coulomb impurity potential to calculate ϵ . It clearly cannot be solved exactly. A common and very convenient approach in similar problems is the variational solution. A family of wave functions must be chosen, in which the boundary conditions (5) and (6) are fulfilled for any value of the variational parameters. We propose here, for estimating the ground-state energy, the following trial function, composed of the unperturbed envelope function F_s , modulated by a separable hydrogenlike confinement function:

$$\mathbf{F} = Ne^{-\rho/a} \begin{bmatrix} e^{(-m_{\Gamma}/b)(z-l)} & 0 \\ 0 & e^{(-m_{X\perp}/b)(z-l)} \end{bmatrix} \mathbf{F}_s, \quad (10)$$

where N is a normalization constant, a and b are the variational parameters. Given that F_s already satisfies the

TABLE I. GaAs and AlAs conduction band edge effective masses (in units of the free electron mass m_e) and energies (in units of meV), with origin chosen at the GaAs Γ minimum, obtained from *Numerical Data and Functional Relationships in Science and Technology*, edited by O. Madelung, Landolt-Börnstein, New Series, Group III, Vol. 22, Pt. a (Springer-Verlag, Berlin, 1987), pp. 63 and 82.

	$m_{\Gamma\perp}$	$m_{\Gamma\parallel}$	$m_{X\perp}$	$m_{X\parallel}$	ϵ_{Γ}	ϵ_X
GaAs	0.067	0.067	0.26	1.8	0	580
AlAs	0.15	0.15	0.19	1.1	1060	160

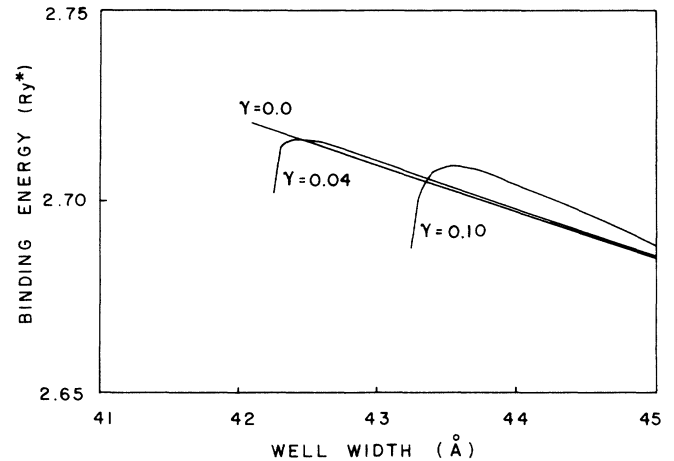


FIG. 3. The binding energy of a shallow impurity in the center of a type-I GaAs/AlAs quantum well as a function of its width for different degrees of valley mixing. The mixing leads to a peak just before the crossover to a type-II well. Note the small length scale in the figure (little less than two atomic layers).

boundary conditions, it is easy to see that so does F . The results we show were obtained by minimizing the expectation value of the energy with respect to a and b .

$$\epsilon = \min_{a,b} \int \mathbf{F}^\dagger \mathbf{H} \mathbf{F} d\mathbf{r}. \quad (11)$$

Figure 2 shows the subband edge (E_s) versus the well width calculated with and without renormalized masses for zero and 10% mixing. The effective masses and band-edge energies used are listed in Table I. The curves show that the mixing leads to a little larger values for E_s , because we effectively add a positive term to the Hamiltonian in the well, where the electron is concentrated. The effect of renormalizing the mass from 0.15 to 0.09 is also

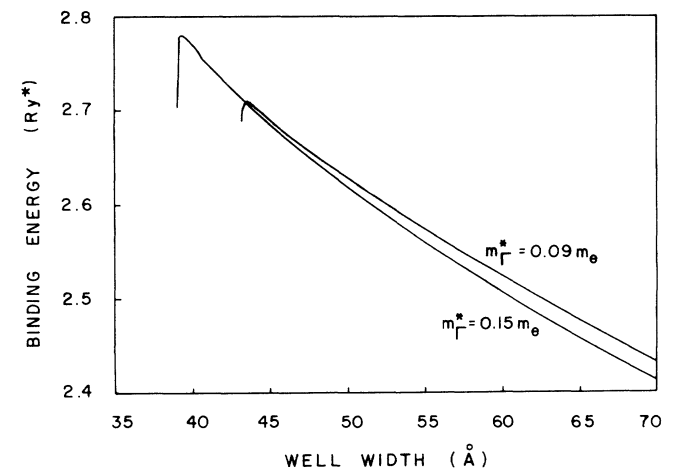


FIG. 4. Dependence of the binding energy on the tunneling AlAs Γ effective mass. The binding energy as a function of the well width is plotted for both effective masses. A renormalized mass is seen to give larger binding energies.

to increase E_s . The shift is fairly the same for all well widths and for broad wells where the probability of finding the electron outside the well is extremely small (0.1%). This indicates that the shift is more due to the change in boundary conditions (6) than the change in the Hamiltonian (2).²⁹ The effect of renormalizing the effective mass is larger than that of including 10% mixing.

Figure 3 shows the binding energy E_b for zero, 4%, and 10% mixing. The curves are only drawn for well widths where the system is type I ($E_s < \epsilon_X \chi_2$). It is clearly seen that the mixing changes the curve qualitatively, introducing a peak for well widths slightly broader than the one for which the crossover occurs. We also note that when the mixing is changed, so is the position of the peak. We understand this by examining Fig. 2, and noting that for 10% mixing, the crossover occurs for a broader well than for zero mixing. The difference, however, is quite small.

In Fig. 4 we show how the binding energy depends on the Γ effective mass in AlAs. The peak appears shifted due again to the shift in the well width where crossover occurs. The renormalized mass gives larger binding energy. This is because when we change the effective mass, we change the boundary conditions (6), and this has the effect of squeezing the electron into the well, closer to the core when the mass is reduced.

Summarizing, we have calculated for the first time the binding energy of a shallow donor in the center of an AlAs/GaAs type-I quantum well including Γ - X mixing. We have found that the mixing leads to a qualitatively new behavior close to the type I-to-type II crossover, but that the effects of mixing are small for most well widths. The position of the peak follows the critical well width for which crossover occurs, and this is again dependent on the renormalized mass.

¹To be precise, there is a small structure near the X point known as the camel's back, which will not be considered here.

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