

Binding energies of acceptors in GaAs-Al_xGa_{1-x}As quantum wells

W. T. Masselink

*Department of Physics and Coordinated Science Laboratory, University of Illinois
at Urbana-Champaign, Urbana, Illinois 61801*

Yia-Chung Chang

*Department of Physics and Materials Research Laboratory, University of Illinois
at Urbana-Champaign, Urbana, Illinois 61801*

H. Morkoç

*Coordinated Science Laboratory and Department of Electrical Engineering University of Illinois
at Urbana-Champaign, Urbana, Illinois 61801*

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We present a variational calculation of acceptor binding energies in a GaAs-Al_xGa_{1-x}As quantum well. The calculation includes the coupling of the top four valence bands of both materials in the multiband effective-mass approximation. Because the quantum-well potential reduces the bulk symmetry, the bulk Γ_8 acceptor ground state splits into Γ_6 and Γ_7 states. The ground-state energies in both symmetries have been calculated for three barrier heights as functions of well width. These calculations for barrier heights corresponding to $x=0.3$ are in excellent agreement with the available experimental data.

Early studies of GaAs-AlGaAs superlattices and quantum-well structures emphasized the energy levels of free carriers in undoped materials.¹ Luminescence from such material is dominated by the recombination of free excitons. Recently, both experimental and theoretical workers have begun to pay attention to lightly doped superlattices.²⁻⁷ In these structures we expect both intrinsic and extrinsic processes. In particular, we expect luminescence from bound-exciton recombination, from acceptor to donor transitions, and from acceptor or donor to band transitions in addition to free-exciton recombination. The photon energies resulting from many of these processes have been calculated using various approximations.

Recently Miller, Gossard, Tsang, and Munteanu have reported photoluminescence resulting from the residual acceptor level to conduction-band transition in GaAs-AlGaAs superlattices.³ The data are only in qualitative agreement with a calculation of the binding energy of a hydrogenic impurity in an infinite well.² Although this type of calculation should be reasonable for donors in wide quantum wells, it does not describe the acceptors appropriately because of the degeneracy of the heavy- and light-hole bands. Although the hole's spatial confinement due to the quantum well lifts this degeneracy, the impurity potential will still be sufficiently

deep to significantly couple the heavy- and light-hole bands. This is different from the exciton case where the bands are usually considered to be completely decoupled.⁸ Furthermore, the valence-band structure is not spherically symmetric (or even cylindrically symmetric in the superlattice) necessitating the inclusion of basis states for the wave function with angular momentum greater than zero. Finally, in order to calculate the binding energy for a specific acceptor, a short-ranged core potential must be included.

In this paper, we report a calculation of the ground-state binding energies of acceptors located in the center of quantum wells of finite depth. We use a multiband effective-mass approximation (EMA) where the hole envelope wave function includes both *s*-like and *d*-like terms. The continuity condition is approximately satisfied in a self-consistent manner. After adding the appropriate short-ranged potential so that the bulk limit calculation agrees with the level due to carbon, the binding energy as a function of well width is in quantitative agreement with the data of Miller *et al.*³

We begin with the coupled effective-mass equations for the ideal acceptor in bulk material. In the case of infinite spin-orbit coupling, the problem reduces to four coupled equations. For four coupled bands degenerate at $k=0$, the most general acceptor Hamiltonian may be written as⁹

$$H = \frac{1}{2m_0}(\gamma_1 + \frac{5}{2}\gamma_2)p^2 - \frac{\gamma_2}{m_0}(p_x^2 J_x^2 + p_y^2 J_y^2 + p_z^2 J_z^2) - \frac{2\gamma_3}{m_0}(\{p_x p_y\}\{J_x J_y\} + \{p_y p_z\}\{J_y J_z\} + \{p_z p_x\}\{J_z J_x\}) - \frac{e^2}{\epsilon_0 r}, \quad (1)$$

where $\{ab\} = (ab + ba)/2$, m_0 is the free-electron mass, \vec{p} is the linear momentum operator, $e^2/\epsilon_0 r$ is the screened Coulomb interaction, and $\gamma_1, \gamma_2, \gamma_3$ are the Luttinger parameters describing the valence band of the material. The kinetic energy term can be written in \vec{k} space as

$$\begin{pmatrix} A_+ & B & C & 0 \\ B^* & A_- & 0 & C \\ C^* & 0 & A_- & -B \\ 0 & C^* & -B^* & A_+ \end{pmatrix},$$

where

$$\begin{aligned} A_{\pm} &= \frac{\hbar^2 \gamma_1}{2m_0} \left[\left(1 \pm \frac{\gamma_2}{\gamma_1} \right) (k_x^2 + k_y^2) + \left(1 \mp \frac{2\gamma_2}{\gamma_1} \right) k_z^2 \right], \\ B &= \frac{\hbar^2 \gamma_1}{2m_0} \left[-2\sqrt{3} \frac{\gamma_3}{\gamma_1} (k_y k_z + i k_z k_x) \right], \\ C &= \frac{\hbar^2 \gamma_1}{2m_0} \left[-\sqrt{3} \frac{\gamma_2}{\gamma_1} (k_y^2 - k_x^2) - 2\sqrt{3} \frac{\gamma_3}{\gamma_1} i k_x k_y \right]. \end{aligned} \quad (2)$$

In order to adapt this Hamiltonian to the quantum-well problem, we propose an additional term

$$H_1 = \begin{cases} 0 & \text{for } |z| < W/2, \\ V & \text{for } |z| \geq W/2, \end{cases} \quad (3)$$

where V is the valence-band discontinuity between the well material and the barrier material and W is the well width. We are assuming that V is a scalar so H_1 does not couple different bands. Although the single-well nature of H_1 makes it more appropriate for completely decoupled quantum wells, this potential will also be appropriate for superlattices with thick barriers because the hole is bound and virtually none of its wave function penetrates the barriers. In this calculation, we take $V = 0.15(\Delta E_g)x$,¹⁰ where ΔE_g is the difference in band gaps at $k=0$ between AlAs and GaAs and x is the mole fraction of the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ barriers.

In order to compare results with experimental data of an acceptor, we include a short-ranged potential of the form $H_C = U \exp[-(r/r_0)^2]$, where $r_0 = 1 \text{ \AA}$. The parameter U can be adjusted so the bulk binding energy agrees with the experimental data for a specific impurity.

As in the bulk acceptor problem, we need all even spherical harmonics in the hole wave function to correctly calculate the ground state. Excellent convergence, however, can be reached by including only s -like and d -like states in the hole envelope wave function. In the bulk, symmetry has been used to reduce the number of d states from 20 (5×4 bands) to 2.¹¹ The presence of the quantum well reduces the symmetry from T_d to D_{2d} by giving the material one preferred direction. The fourfold degenerate Γ_8 ground state splits into twofold degenerate states: Γ_6 and Γ_7 .

In order to determine the D_{2d} trial wave functions as has been done in the T_d symmetry, we need to couple the fourfold degenerate valence band with the s -like or d -like envelope wave function. Each wave function will then be a product of either an $l=0$ or $l=2$ polynomial and a spin- $\frac{3}{2}$ spinor. In the bulk, the four spin- $\frac{3}{2}$ spinors are simply the four degenerate Γ_8 states. In order to determine how these spinors transform in the D_{2d} double group, we must construct both the T_d Γ_8 states and the D_{2d} Γ_6 and Γ_7 states by coupling the spin- $\frac{1}{2}$ hole with the $l=1$ valence band. In D_{2d} , $D_{1/2} \times D_1 = \Gamma_6 + 2\Gamma_7$, where D_L is the L th representation of the full rotation group. One of these Γ_7 states is split off by the spin-orbit coupling leaving $\Gamma_6 + \Gamma_7$ (each doubly degenerate). A detailed analysis of the coupling using the coupling coefficients found in Ref. 12 reveals that $\Gamma_8^{3/2} \rightarrow \Gamma_7^{-1/2}$, $\Gamma_8^{1/2} \rightarrow \Gamma_6^{1/2}$, $\Gamma_8^{-1/2} \rightarrow \Gamma_6^{-1/2}$, and $\Gamma_8^{-3/2} \rightarrow \Gamma_7^{1/2}$. Therefore the $\Gamma_7^{-1/2}$ s -like state under D_{2d} is

$$\begin{pmatrix} S \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \quad (4)$$

which is identical to the $\Gamma_8^{3/2}$ s state under T_d .

To find the d states, we must consider the product $(\Gamma_6 + \Gamma_7) \times (\Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5)$ since in the D_{2d} group, a d state splits into $\Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5$. We find

$$(\Gamma_6 + \Gamma_7) \times (\Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5) = 5\Gamma_6 + 5\Gamma_7.$$

Thus there will be five doubly degenerate d -like states of

each symmetry. First, we will consider the Γ_7 solution. Because we may choose either the $\Gamma_7^{1/2}$ or $\Gamma_7^{-1/2}$ states, and already have the $\Gamma_7^{-1/2}$ s state, we will find the five $\Gamma_7^{-1/2}$ d -like states. They are

$$\begin{aligned} {}^1\Gamma_7^{-1/2} &= \begin{pmatrix} 0 \\ \sqrt{3}/2(x^2 - y^2) \\ 0 \end{pmatrix}, & {}^2\Gamma_7^{-1/2} &= \begin{pmatrix} 0 \\ 0 \\ ixy \\ 0 \end{pmatrix}, \\ {}^3\Gamma_7^{-1/2} &= \begin{pmatrix} 0 \\ iz(x + iy) \\ 0 \\ 0 \end{pmatrix}, & {}^4\Gamma_7^{-1/2} &= \begin{pmatrix} z^2 - \frac{1}{2}(x^2 + y^2) \\ 0 \\ 0 \\ 0 \end{pmatrix}, \\ {}^5\Gamma_7^{-1/2} &= \begin{pmatrix} 0 \\ 0 \\ 0 \\ iz(x - iy) \end{pmatrix}. \end{aligned} \quad (5)$$

Since the Hamiltonian contains terms like $(k_y k_z + ik_z k_y)$ but no $(k_y k_z - ik_z k_x)$ -like terms, the ${}^5\Gamma_7^{-1/2}$ state is not coupled to the other states and can be discarded. Therefore we include the single s state and the first four d states presented above. Similarly, for the Γ_6 solution, we find a $\Gamma_6^{1/2}$ s -like state and five d -like states but ignore the fifth. These states can be obtained from those listed above by simply exchanging the first and second components and exchanging the third and fourth components.

All of these wave functions are automatically continuous across the interface. If we were using a Hamiltonian in which the effective-mass parameters were different in the two materials, such a choice of basis would result in the Hamiltonian matrix being non-Hermitian. As it stands now, however, this problem does not exist. It would be preferable to define the basis so that the continuity condition is satisfied and use the parameters of each material in its own spatial region. Because of the multiband nature of this problem and because of the reduced symmetry, this method would be extremely cumbersome. Rather, we take the difference in band structure and dielectric constant into account by solving the problem twice: once assuming the parameters of the one material, another time assuming the parameters of the other material, and then interpolating between the two. This should be a good approximation since the valence-band parameters and dielectric constants do not differ much in the two materials.

For each symmetry we solve the EMA Schrödinger equation $H\psi = E\psi$ by expanding the acceptor wave function ψ in a basis set containing five types of states described in (4) and (5). For each type of basis state, we use seven anisotropic Gaussian-type wave functions, so that $\langle \bar{r} | s \rangle = \exp[-\alpha_i(x^2 + y^2 + \mu z^2)]$, where the α_i are chosen to cover a large physical range. The parameter μ is an anisotropy factor which allows the wave function to be compressed in the z direction. Similarly, $\langle \bar{r} | z^2 \rangle = z^2 \exp[-\alpha_i(k^2 + y^2 + \mu z^2)]$, etc. Since there are five types of states and seven values of α_i for each type, solving Schrödinger's equation for a given symmetry and for a given μ means solving a 35×35 secular equation. This is done numerically with the use of a high-speed computer. The value of μ is varied until the energy E is minimized. The resulting lowest-energy eigenvalue is the variational acceptor ground-state energy as measured from the bulk valence-band edge. In order to calculate the binding energy for the acceptor, we also calculate the quantized heavy- and

light-hole subband edges as measured from the bulk valence-band edge using the same Hamiltonian with the impurity potential excluded. The Γ_7 acceptor binding energy is the difference between the Γ_7 acceptor energy and the highest heavy-hole subband edge, and the Γ_6 acceptor binding energy is the difference between the Γ_6 acceptor energy and the highest light-hole subband edge.

As previously noted, in order to account for the difference in effective-mass parameters and dielectric constants in the two materials, the problem is solved twice for each well width and barrier composition. We define f_1 as the fraction of hole envelope wave function in the GaAs assuming the GaAs parameters, and f_2 as the fraction of hole envelope wave function in the GaAs assuming the AlGaAs parameters. The actual fraction of hole wave function in the GaAs, f , requires $f = ff_1 + (1-f)f_2$. Thus $f = f_2 / (1 + f_2 - f_1)$. The actual binding energy then is $E = fE_1 + (1-f)E_2$ where E_1 is the energy assuming the GaAs parameters and E_2 is the energy assuming the AlGaAs parameters.

We study GaAs-Al_xGa_{1-x}As quantum wells with three different alloy compositions: $x=0.05$, $x=0.30$, and $x=1.0$. The Luttinger parameters and dielectric constants are taken to be¹³

$$\epsilon_0 = 12.35, \gamma_1 = 7.65, \gamma_2 = 2.41, \gamma_3 = 3.28$$

for GaAs and

$$\epsilon_0 = 9.80, \gamma_1 = 4.04, \gamma_2 = 0.78, \gamma_3 = 1.57$$

for AlAs. For the alloys, we use a linear interpolation between those of GaAs and of AlAs for all four parameters. The calculated acceptor binding energies as measured from the appropriate hole subband edge are shown for the three alloy compositions and both symmetries (Γ_6 and Γ_7) as functions of the well width in Fig. 1. In all cases, there is a characteristic well width which maximizes the acceptor binding energy for a given symmetry. This is due to the finite barrier and is similarly seen in quantized donor^{5,7} and exciton⁸ calculations. For smaller alloy compositions, we find that the maximum occurs at larger values of the well width. Hence, to experimentally detect the position of this maximum, the quantum well with smaller alloy composition will be a better choice.

As the well width approaches zero, the acceptor binding energy for both symmetries approaches that of the acceptor binding energy in the bulk AlGaAs, since with zero well width all that is left is bulk AlGaAs. Increasing the well width from zero, the symmetry is lowered and this single level splits into the Γ_7 and Γ_6 levels; the wave functions of the two levels are predominantly derived from the heavy- and light-hole bands, respectively. The binding energy tends to be greater and its maximum occurs at a larger well width for the Γ_6 solution than for the Γ_7 solution. This is understandable since the Γ_6 energy is measured from the highest light-hole subband which is always greater in energy than the highest heavy-hole subband from which the Γ_7 energy is measured. Of course, the total Γ_6 energy is also greater than the total Γ_7 energy, but usually the difference in subband energy is greater than this difference. Therefore the Γ_6 binding energy is usually greater than the Γ_7 binding energy except for very small well widths (≤ 40 Å) where the Γ_6 binding energy is slightly lower. For well widths greater than about 200 Å, the total acceptor energy is essen-

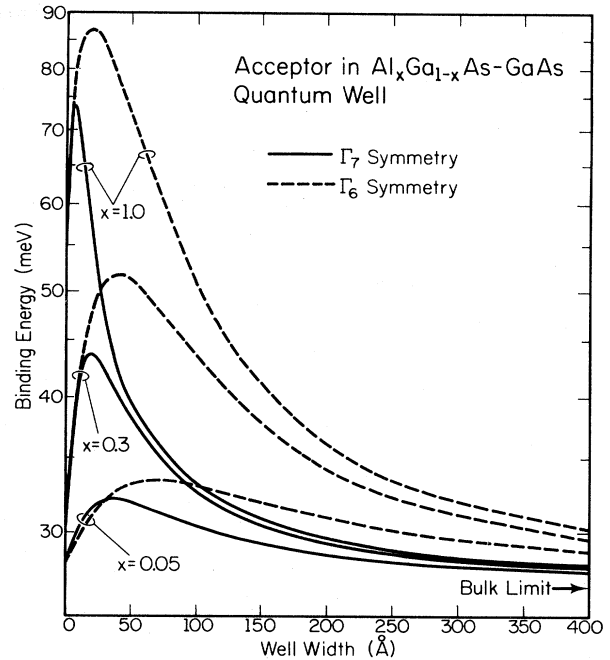


FIG. 1. Energies of the center-doped ideal acceptor ground states as functions of well width for three barrier heights and both symmetries. The Γ_6 binding energy is measured from the top of the light-hole subband and the Γ_7 binding energy is measured from the top of the heavy-hole subband.

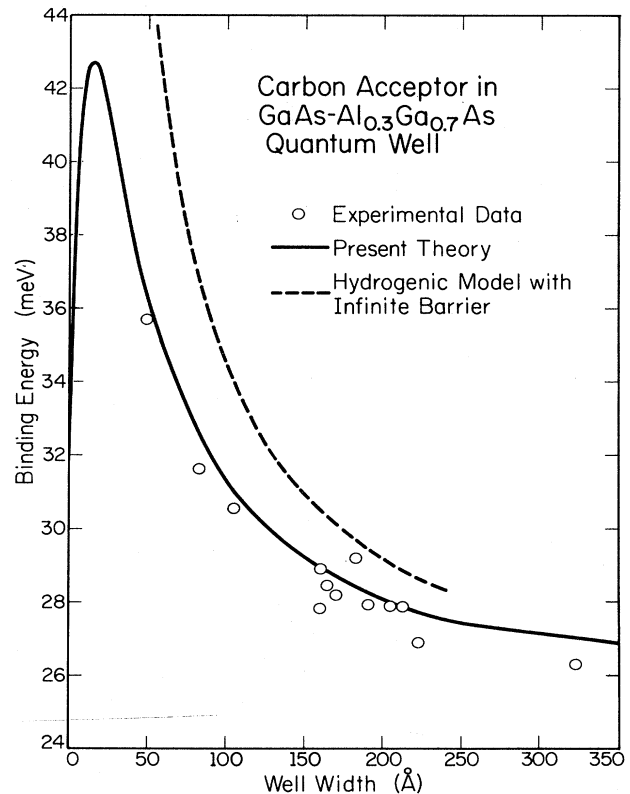


FIG. 2. Energy of the Γ_7 center-doped carbon-acceptor ground state as a function of well width (solid), the infinite barrier hydrogenic binding energy of Ref. 2 (dashed), and experimental data (circles) of Ref. 3 for the $x=0.3$ barrier height.

tially the same as in the bulk, but the Γ_6 and Γ_7 binding energies are still somewhat different because of the difference in subband energies. Thus, for wide wells, the Γ_7 or Γ_6 binding energy is essentially the bulk acceptor binding energy plus the heavy- or light-hole subband energy measured from the bulk valence-band edge. Finally, as the well width approaches infinity, the acceptor binding energy for both symmetries converges to 27.1 meV. The described splitting of the original Γ_8 solution cannot, of course, be described in a hydrogenic calculation.

For comparison with the data of Miller *et al.*³ for a carbon acceptor, the core potential was added to the Hamiltonian as described: $H_c = U \exp[-(r/r_0)^2]$. By the use of $U = 8.00$ eV and $r_0 = 1.0$ Å, the calculated bulk binding energy was the same as the experimentally measured value (26.0 meV). The $x = 0.30$ case was again calculated with H_c included. The Γ_7 symmetry solution along with Miller's³ data and Bastard's² hydrogenic calculation using an infinite well is shown in Fig. 2. As expected, the infinite-well calculation predicts deeper binding than is actually observed. By correctly including the top four valence bands and allowing the wave function to penetrate into the finite barrier, the acceptor binding energy is substantially lower and in excellent agreement with the data. We are presently experimentally

measuring the acceptor binding energy for quantum wells selectively doped on center and on edge using molecular beam epitaxy (MBE). We expect to extend this theory to allow the calculation of off-center acceptor binding energies.

Summarizing, we have calculated the acceptor binding energy for center-doped GaAs-Al_xGa_{1-x}As quantum wells over a range of x and well widths. The calculation is variational in the EMA using a flexible basis and includes the coupling of the top four valence bands. After including the short-ranged potential appropriate for the carbon acceptor, the agreement of the calculation with available data is excellent. More detailed results including the energies for several different acceptors will be reported in the future.

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¹For a review, see R. Dingle, in *Festkörperprobleme*, Advances in Solid State Physics, Vol. 15, edited by H. J. Queisser (Pergamon-Vieweg, Braunschweig, 1975), pp. 21-48.

²G. Bastard, Phys. Rev. B **24**, 4714 (1981).

³R. C. Miller, A. C. Gossard, W. T. Tsang, and O. Munteanu, Phys. Rev. B **25**, 3871 (1982).

⁴R. C. Miller, A. C. Gossard, W. T. Tsang, and O. Munteanu, Solid State Commun. **43**, 519 (1982).

⁵C. Mailhot, Y. C. Chang, and T. C. McGill, J. Vac. Sci. Technol. **21**, 519 (1982); Phys. Rev. B **26**, 4449 (1982).

⁶B. Lambert, B. Deveaud, A. Regreny, and G. Talalaeff, Solid State Commun. **43**, 443 (1982).

⁷R. L. Greene and K. K. Bajaj, Solid State Commun. **45**, 825 (1983).

⁸R. L. Greene and K. K. Bajaj, Solid State Commun. **45**, 831 (1983).

⁹J. M. Luttinger, Phys. Rev. **102**, 1030 (1956).

¹⁰R. Dingle, A. C. Gossard, and W. Wiegmann, Phys. Rev. Lett. **34**, 1327 (1975).

¹¹D. Schechter, J. Phys. Chem. Solids **23**, 237 (1962).

¹²G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, *Properties of the Thirty-Two Point Groups* (MIT, Cambridge, MA, 1963).

¹³As compiled by J. C. M. Henning, J. J. P. Noijen, and A. G. M. de Nijs, Phys. Rev. B **27**, 7451 (1983).