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Binding energy of the $2p_0$-like level of a hydrogenic donor in GaAs-Ga$_{1-x}$Al$_x$As quantum-well structures

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Recently we reported a calculation of the binding energy of the $2p_0$-like level of hydrogenic donor associated with the first conduction subband in a GaAs-Ga$_{1-x}$Al$_x$As quantum-well structure. It was found that the value of the binding energy of this level decreased as the well width was reduced, and became zero for a well width of about 650 Å. In this Brief Report we present results which demonstrate that this peculiar behavior of the $2p_0$ state is due to the fact that it is closely associated with the second electron subband, and remains bound with respect to it (with increasing binding energy) as the well width is reduced.

I. INTRODUCTION

Epitaxial crystal-growth techniques such as molecular-beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOCVD) have led to the creation of systems of alternating layers of two different semiconductors with controlled thicknesses and sharp interfaces. The effects of the resulting quantum wells upon shallow impurity states have become a subject of lively interest. GaAs-Ga$_{1-x}$Al$_x$As quantum-well structures have been most commonly studied.[1-6] As is well known, the discontinuity of the conduction and valence bands at the interfaces in these structures results in the breaking of the bulk conduction and valence bands into subbands. In Ref. 3 (hereafter referred to as I) we presented binding energies with respect to the first conduction subband of a shallow donor at the center of a quantum well. As in that paper, we refer to these states with nomenclature taken from their hydrogenic (large well width) limits ($1s$, $2s$, $2p\pm$, and $2p_0$). The $2s$ and $2p\pm$ states showed behavior qualitatively similar to the ground state; that is, their binding energies increased with decreasing well width (L) over the range of L studied. The $2p_0$ state showed remarkably different behavior, decreasing in energy rapidly with decreasing L, becoming unbound (with respect to the first electron subband) at a rather large value of L ($L \simeq 6.5a_0$, where a_0 is the effective Bohr radius in bulk GaAs, $a_0 \simeq 100$ Å). In this Brief Report we present results which demonstrate that this behavior of the $2p_0$ state is due to the fact that it is closely associated by symmetry with the second electron subband, and remains bound with respect to it (with increasing binding energy) as L is decreased.

II. THEORY

As noted in I, in the effective-mass approximation the Hamiltonian for an electron bound to a shallow donor in a quantum well is given by

$$H = \frac{-1}{m^*}\nabla^2 - \frac{2}{r} + V_B(z) \ . \tag{1}$$

The quantum-well potential is given as

$$V_B(z) = \begin{cases} 0, & |z| < L/2 \ , \\ V_0, & |z| > L/2 \ , \end{cases} \tag{2}$$

where L is the width and V_0 the height of the quantum well. The position of the impurity atom is assumed to be located at the center of the well. Equations (1) and (2) are given in dimensionless form, such that the unit of length is the effective Bohr radius, energy is given in terms of the effective rydberg, and the effective mass is in terms of the bulk effective mass of the well material. For GaAs, these quantities are 98.7 Å, 5.83 meV, and $0.067m_e$, respectively.

As before, we assume a variational wave function of the form (in cylindrical coordinates ρ, z, and ϕ)

$$\Psi(\rho,z,\phi) = f(z)G(\rho,z,\phi) \ . \tag{3}$$

The function $f(z)$ is a solution of the one-dimensional square-well problem with the potential of Eq. (2), and $G(\rho,z,\phi)$ is a function of electron-donor ion relative coordinates, which we will examine presently. In I, the ground-state solution for the square-well problem was approximated by a series of Gaussians in z, with accuracy to within 0.005 effective rydbergs. This allowed us to obtain binding energies of the ground and several excited states with respect to the first subband.

For this work we take $f(z)$ to be the analytic solution for the first excited state in the one-dimensional quantum well; that is, the unnormalized expression is

$$f(z) = f_2(z) = \begin{cases} -Be^{\kappa z}, & z < -L/2 \ , \\ \sin(kz), & \frac{-L}{2} < z < L/2 \ , \\ Be^{-\kappa z}, & z > L/2 \ . \end{cases} \tag{4}$$

The parameter k is determined by the first excited state energy of the one-dimensional square well. B and κ are fixed by the matching conditions used at the GaAs-Ga$_{1-x}$Al$_x$As interfaces. These will be mentioned presently. For later use we give the one-dimensional square-well ground-state solution here also:

$$f_1(z)=\begin{cases}\cos(kz), & |z|<L/2\ ,\\ B'e^{-\kappa'|z|}, & |z|>L/2\ .\end{cases} \tag{5}$$

For the relative coordinate function $G(\rho,z,\phi)$ we use a series of Gaussians very similar to what we used in I. With the donor at the center of the well, parity is a good quantum number. Thus, we write $G(\rho,z,\phi)$ as

$$\begin{aligned}G(\rho,z,\phi)&=G_{mq}(\rho,z,\phi)\\ &=z^q\rho^{|m|}e^{im\phi}\sum_{i,j}A_{ij}\exp(-\alpha_i\rho^2-\beta_j z^2)\ .\end{aligned} \tag{6}$$

The integer m is the component of the angular momentum (in units of $\hbar$) along the axis of symmetry, and $m+q$ (where $q=0,1$), together with $f(z)$, defines the parity of the state. In I, the states that we labeled 1s, 2s, $2p\pm$, and $2p_0$ correspond to the following m, q pairs:

$1s, 2s$	$m=q=0$	(even parity)
$2p\pm$	$m=\pm1, q=0$	(odd parity)
$2p_0$	$m=0, q=1$	(odd parity)

Here, however, the function $f_2(z)$ is odd in z, which makes the $m=q=0$ states odd-parity states. We will not consider the other cases.

For the calculations of this paper we take the set of nonlinear variational parameters $\{\alpha_i\}=\{\beta_i\}$ from the work of Huzinaga,[7] who did a systematic study of the use of Gaussian basis sets in the calculations of atomic energy levels. The set we used is given in Table I; they yield energies accurate in the hydrogenic limit to within 0.001 effective rydbergs. The linear variational parameters A_{ij} are determined from the solution of the usual matrix eigenvalue equation:

$$\underline{H}\psi=E\underline{U}\psi\ . \tag{7}$$

The symbol ψ represents a vector made up of the different basis functions in which we have expanded $\Psi(\rho,z,\phi)$. The basis function for a given i,j pair is

$$z^q\rho^{|m|}e^{im\phi}f_2(z)e^{-\alpha_i\rho^2}e^{-\alpha_j z^2}\ .$$

$\underline{H}$ and $\underline{U}$ are the Hamiltonian and overlap matrices between the elements of ψ. We restrict the size of $\underline{H}$ and $\underline{U}$ to 13×13 by requiring $A_{ij}=0$ for $|i-j|>1$. This means that the function $G_{mq}(\rho,z,\phi)$ in Eq. (6) has 13 terms. Note that it is not separable in ρ and z, even though the individual terms are separable.

The choice of variational wave function given by Eqs. (3), (4), and (6) allows us to calculate accurate Coulomb binding energies by subtracting the eigenvalues of H from the one-dimensional well energy. A similar wave function with $f_2(z)$ replaced by $f_1(z)$ allows us to calculate binding energies with respect to the first subband edge.

For the results to be presented in Sec. III we have taken the effective mass in the $Ga_{1-x}Al_xAs$ barrier to be dependent upon x as[2] $m^*=(1+1.24x)$, in units of the bulk GaAs electron effective mass $(0.067m_e)$. The dielectric constant is assumed to be equal to the bulk GaAs value for both semiconductors. The variational wave function Ψ (i.e., the effective mass envelope function) and its derivative we assumed continuous at the interfaces. As noted by Zhu and Kroemer,[8] these matching conditions should give good results for $GaAs\text{-}Ga_{1-x}Al_xAs$ systems. The probability density interpretation of $|\Psi|^2$ must be modified somewhat in the barrier material,[8] but that does not concern us here.

TABLE I. Values of the nonlinear variational parameters used (Ref. 7).

α_i	13.4	2.01	0.454	0.123	0.0267

III. RESULTS AND DISCUSSION

In this section we concentrate our attention on three particular odd-parity states, which we label by their quantum numbers m:

$$\Psi_0(\rho,z,\phi)=f_2(z)\sum_{i,j}A_{ij}\exp(-\alpha_i\rho^2-\alpha_j z^2) \tag{8}$$

and

$$\Psi\pm(\rho,z,\phi)=f_1(z)e^{\pm i\phi}\sum_{i,j}B_{ij}\exp(-\alpha_i\rho^2-\alpha_j z^2)\ . \tag{9}$$

Note that Ψ_0 (which is odd in z) is associated with the second subband and $\Psi\pm$ (even in z) are associated with the first subband, due to the functions $f_2(z)$ and $f_1(z)$. In Fig. 1 we plot the total energies (solid curves) of these states as a function of L, taking the bottom of the quantum well (bulk GaAs band edge) as our zero energy reference. Also plotted in the figure are the first and second subband

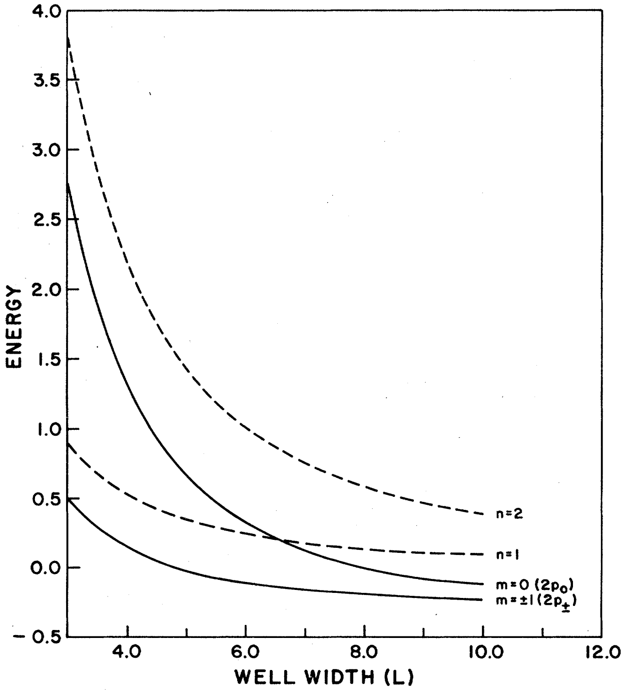

FIG. 1. Variation of the total energies of the $2p\pm$ and $2p_0$-like states (solid lines) and of the first $(n=1)$ and second $(n=2)$ electron subband levels as a function of the GaAs well size (L). The Al concentration x is 0.3. All energies are expressed in terms of an effective rydberg (5.83 meV) and all distances in terms of Bohr radius (98.7 Å).

edges (dashed curves). The Coulomb binding energies mentioned earlier can be obtained by subtracting the appropriate band-edge energy from the chosen total energy.

The energies of the states represented by Eqs. (8) and (9) lie below the corresponding subband edge for the range of L shown in Fig. 1. Note that the odd-parity $m=0$ state also lies below the first subband edge for $L \gtrsim 6.5$. The crossing point is virtually the same point that we found the $2p_0$ state of I to become unbound with respect to the first subband. This suggests that the $2p_0$ state of I, described by the variational wave function

$$\Psi_0'(\rho,z,\phi)=f_1(z)z\sum_{i,j}A_{ij}\exp(-\alpha_i\rho^2-\alpha_j z^2) \qquad (10)$$

is the same as the odd-parity $m=0$ state represented by Eq. (8). This should not be surprising since $f_2(z)$ and $zf_1(z)$ both vary linearly with z for $z << L$.

We have verified this expectation by directly comparing the energies obtained from the variational wave functions of Eqs. (8) and (10). For $L > 6.5$ the energies are the same to better than 1%. For $L < 6.5$, they begin to deviate significantly, because Ψ_0 of Eq. (8) is a much better variational wave function than Ψ_0' at small well widths. Our conclusion is that the $2p_0$ state in I that became "unbound" appeared to do so because it is actually a bound state associated with the second, rather than the first subband. The fact that the variational trial functions of Eqs. (8) and (10) give virtually identical energies for $L > 6.5$ suggests that the function $G_{mq}(\rho,z,\phi)$ has sufficient flexibility to handle any subband mixing that may occur in large quantum wells and, therefore, should give very good energy estimates.

However, for $L \lesssim 6.5$ there are continuum states of the first subband which are resonant with bound states associated with the second subband. In the ideal case with the donor at the center of the well these states are not mixed by the Coulomb potential because of their different parities. Nevertheless, in a real situation, where the donor is not exactly at the center, there will be nonvanishing Coulomb matrix elements between the second subband bound states and the first subband continuum. This can significantly shorten the lifetimes of the (quasi)bound states associated with the second subband. This broadening effect, when combined with the broadening due to the fact that the energy is strongly dependent upon the position of the donor, may make it difficult to observe the binding energy of the $2p_0$-like state in quantum wells with $L \lesssim 6.5$ effective Bohr radii.

IV. CONCLUSIONS

The odd-parity $m=0$ state ($2p_0$), whose binding energy with respect to the first subband drops sharply with decreasing L,[3] behaves in that way because it is a bound state closely associated with the second subband. Moreover, for $L \gtrsim 6.5a_0$ we obtain virtually identical energies for the $2p_0$ state, regardless of whether we factor the one-dimensional square-well ground-state solution $f_1(z)$, or first excited state solution $f_2(z)$, out of our variational trial function. This indicates to us that the series of z Gaussians in our trial wave function has sufficient flexibility to handle subband mixing which may occur for large L values. For $L < 6.5a_0$, resonance between the continuum states of the first subband and the quasibound states just below the second subband may prevent the binding energy of the latter from being measured.

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