

Effect of magnetic field on the energy levels of a hydrogenic impurity center in GaAs/Ga_{1-x}Al_xAs quantum-well structures

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(Received 18 July 1984)

We have calculated the binding energies of the ground ($1s$ -like) and excited ($2p_{\pm}$ -like) states of a hydrogenic donor associated with the first subband in a GaAs quantum well, sandwiched between two semi-infinite layers of Ga_{1-x}Al_xAs. Results have been obtained as a function of the potential-barrier height (or equivalently of Al concentration x) and the size of the quantum well in the presence of an arbitrary magnetic field. We have considered the two cases of donor at the center and at the edge of the well. The applied magnetic field is taken to be parallel to the axis of growth of the quantum-well structure. We have used a variational approach in which the trial wave functions are expanded in terms of appropriate Gaussian basis sets. For a given value of the magnetic field, the binding energies are found to be larger than their values in a zero magnetic field.

INTRODUCTION

With recent advances in epitaxial crystal-growth techniques such as molecular-beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOCVD), it has become possible to grow systems of alternate layers of either two different materials (heterostructures) or of the same material with different doping properties, having controlled thickness and sharp interfaces. These relatively new one-dimensional periodic structures, with dimensions which can approach the atomic spacings of the constituent materials of which they are composed, are referred to as superlattices. Among the most extensively studied superlattices is the one consisting of alternate layers of GaAs and Ga_{1-x}Al_xAs. Depending on the Al content in Ga_{1-x}Al_xAs, its band gap can be made considerably larger than that of GaAs, thus leading to discontinuities of the conduction- and valence-band edges at the interfaces between GaAs and Ga_{1-x}Al_xAs. For Al concentration less than about 40% ($x \lesssim 0.4$), Ga_{1-x}Al_xAs has a direct band gap at the Γ point.¹ The conduction- and the valence-band discontinuities at the interfaces have been suggested to be about 85 and 15%, respectively, of the direct-band-gap difference between the two semiconductors.² This leads to the formation of quantum wells in the GaAs layers.

The study of the behavior of hydrogenic impurity centers located in a quantum well consisting of a single layer of GaAs surrounded by two semi-infinite (> 200 Å in practice) layers of Ga_{1-x}Al_xAs, has been a subject of considerable interest in recent years. Bastard,³ for instance, has calculated the binding energy of the ground state of a hydrogenic donor associated with the lowest electron subband level, as a function of GaAs well size (L) and the position of the impurity ion. He used a varia-

tional approach and assumed infinite potential at the interfaces. Mailhiot *et al.*⁴ and Greene and Bajaj⁵ have independently calculated the binding energies of the ground state and of several low-lying excited states of a hydrogenic donor as a function of L for finite values of the potential barriers. Both of these groups used variational techniques and found essentially the same results. Tanaka *et al.*⁶ have calculated the binding energy of the ground state of a donor in a quantum well with asymmetric potential barriers. They have also considered the case in which the positive ion of the impurity atom is located in the surrounding Ga_{1-x}Al_xAs layer. The effect of non-parabolicity of the conduction band on the energy levels of a hydrogenic donor in a quantum well has been investigated by Chaudhuri and Bajaj.⁷ Recently, Masselink *et al.*⁸ have calculated the binding energy of the ground state of an effective-mass acceptor as a function of quantum-well size taking into account the complex nature of the valence-band structure. The effect of thin (< 50 Å) Ga_{1-x}Al_xAs surrounding layers on the energy levels of a hydrogenic donor in a multiquantum well structure has been considered by Chaudhuri.⁹

In this paper we report a calculation of the binding energies of the ground state ($1s$ -like) and excited states ($2p_{\pm}$ -like), referred from hereon as $1s$ and $2p_{\pm}$, respectively, of a hydrogenic donor associated with the first subband in GaAs/Ga_{1-x}Al_xAs quantum well in the presence of a magnetic field. Our results are given as a function of the potential-barrier height (or, equivalently, the x value) and the size of the quantum well. We consider the two cases of the impurity atom located at the center and at the edge of the well. In addition, the applied magnetic field is taken to be parallel to the axis of growth of the quantum-well structure. We follow a variational approach in which the trial wave functions used are expanded in terms of ap-

appropriate Gaussian basis sets. As expected, we find that for a given value of the magnetic field, the binding energies are larger than their values in zero magnetic field.

THEORY

Within the framework of an effective-mass approximation, the Hamiltonian of a hydrogenic donor in a GaAs quantum well, in the presence of an applied magnetic field, can be written as

$$H = \frac{1}{2m_e^*} \left[\vec{p} - \frac{e}{c} \vec{A} \right]^2 - \frac{e^2}{\epsilon_0 r} + V_B(z), \quad (1)$$

where the barrier potential $V_B(z)$ is taken to be a square well of height V_0 and width L ,

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

The position of the electron is denoted by r , where $r = [\rho^2 + (z - z_I)^2]^{1/2}$, ρ being the distance in the x - y plane, and z_I is the z coordinate of the impurity atom. The quantity m_e^* is the effective mass, which is different in the two semiconductors. The values of the static dielectric constant ϵ_0 are assumed to be the same in GaAs and $\text{Ga}_{1-x}\text{Al}_x\text{As}$. This is a good approximation as seen by comparing the results of Mailhot *et al.*,⁴ who take into account the different effective masses and dielectric constants in GaAs and $\text{Ga}_{1-x}\text{Al}_x\text{As}$ with those of Greene and Bajaj,⁵ who use the same values of these parameters.

The vector potential \vec{A} is defined as

$$\vec{A} = \frac{1}{2} \vec{B} \times \vec{r}. \quad (3)$$

Using a cylindrical coordinate system where the magnetic field is applied along the direction of growth (assumed to be the z axis) the Hamiltonian can be expressed as

$$H = - \left[\frac{m^*}{m_e} \right] \nabla^2 - \frac{2}{r} + \gamma L_z + \frac{1}{4} \gamma^2 \rho^2 + V_B(z). \quad (4)$$

Here we have used the effective Bohr radius in GaAs, $a_0 = \hbar^2 \epsilon_0 / m^* e^2$, as our unit of length and the effective rydberg $R = e^2 / 2 \epsilon_0 a_0$ as our unit of energy. For GaAs ($m^* = 0.067 m_e$, $\epsilon_0 = 12.5$) these quantities are $a_0 = 98.7 \text{ \AA}$ and $R = 5.83 \text{ meV}$. In Eq. (4) L_z is the z component of the angular momentum operator (in units of \hbar) and γ is a dimensionless measure of the magnetic field, defined as

$$\gamma = \frac{e \hbar B}{2 m^* c R}. \quad (5)$$

We assume for these calculations that conduction-band discontinuity or the barrier height V_0 in Eq. (2) is 85% of the total band-gap difference between the two semiconductors. We have determined the band-gap difference from the following empirical expression:¹

$$\Delta E_g = 1.155x + 0.37x^2 \text{ eV}. \quad (6)$$

We calculated the eigenvalues of the Hamiltonian described by Eq. (4) following a variational approach. For

commonly used values of x and L , the barrier height is much larger than the effective rydberg. Thus, the energy associated with the Coulomb interaction will, except for large well widths, be small compared to the subband energy in the square well. Because of this it is helpful to explicitly factor the solution to the ground state of an electron in the one-dimensional square well, $f(z)$, out of the variational donor wave function ψ :

$$\psi = f(z) G(\rho, z, \phi), \quad (7)$$

where $G(\rho, z, \phi)$ describes the internal states of the donor and $f(z)$ is the solution to the square-well problem, given as

$$f(z) = \begin{cases} \cos(kz), & |z| \leq L/2 \\ A e^{-\kappa|z|}, & |z| > L/2. \end{cases} \quad (8)$$

The parameter k is determined from the energy of the first subband and the quantities A and κ are determined by the matching conditions at the interface. It is assumed that $f(z)$ and $(m^*/m_e^*) \partial f / \partial z$ are continuous across the interface. As discussed in Sec. III, however, the results are not very sensitive to the matching conditions chosen, except at small ($\leq 25 \text{ \AA}$) well widths.

For wells less than several Bohr radii in width, the factorization in Eq. (7) is particularly appropriate because it enables the separation of the relatively large square-well energy that would otherwise overwhelm the smaller Coulomb energy contribution. For large well widths where the energy of the subband is comparable to the Coulomb contribution, the factorization is of little or no value because the higher subbands can be mixed with the lowest subband by the Coulomb potential. This, however, does not cause any significant problem provided the function $G(\rho, z, \phi)$ has sufficient variational flexibility.

The Hamiltonian of our system [Eq. (4)] has cylindrical symmetry. The z component of the angular momentum is therefore a good quantum number and the ϕ dependence of the wave function thus has the form $\exp(im\phi)$, where m is an integer. If the donor impurity ion is located at the center of the well, the Hamiltonian is also invariant under reflections through the origin. The wave function then has a definite parity. Using this knowledge, the function $G(\rho, z, \phi)$ can be written in the form

$$G(\rho, z, \phi) = \rho^{|m|} e^{im\phi} \sum_{i,j} A_{ij} G_{ij}(\rho, z), \quad (9)$$

when the donor is located at the center of the well. The basis functions $G_{ij}(\rho, z)$ are taken to be the products of Gaussians in ρ and z variables:

$$G_{ij}(\rho, z) = e^{-\alpha_i z^2} e^{-(\alpha_j + \beta) \rho^2}. \quad (10)$$

For the off-center case we replace z by $z - z_I$ in the G_{ij} functions. (When the donor is at the edge, $z_I = \pm L/2$.) This choice is made because of the success of a similar basis set which Aldrich and Greene¹⁰ used to solve the problem of a hydrogen atom in a magnetic field. They found that the use of a Gaussian basis set yielded good results for the ground and several excited states throughout the range $0 \leq \gamma \leq 10$.

TABLE I. Values of the parameter α_i used for the ground state ($m=0$) and $2p$ -like states ($m=1$) in units of the inverse effective Bohr radius (a_0).

$m=q=0$	$m=\pm 1, q=0$
13.4	0.734
2.01	0.174
0.454	0.0557
0.123	0.0202
0.0267	

The set of parameters α_i used in this work are given in Table I. These are taken from the results of Huzinaga,¹¹ who performed a detailed study of the use of Gaussian basis functions in the calculations of the energy levels of a hydrogen atom. This set of α_i gives energies for the $1s$, $2s$, and $2p$ free-hydrogen-atom states accurate to within 0.001 Ry. The parameter β was varied in each case to minimize the energy and is primarily determined by the size of the magnetic field. Calculations were also made using β as a multiplicative variational parameter in the argument of the ρ Gaussian, rather than the additive one of Eq. (10). The results were poorer (gave smaller binding energies) by up to 10%, particularly for large magnetic field strengths.

The energies were obtained by solving the matrix eigenvalue equation,

$$\underline{H}\psi = E\underline{U}\psi, \quad (11)$$

where \underline{H} and \underline{U} are the Hamiltonian and overlap matrices, respectively. For numerical reasons we restricted the number of basis functions by requiring $A_{ij}=0$ for $|i-j| > 1$. This has negligible effect on the energies obtained. For the ground state ($m=0$) the number of basis functions used (and hence the order of the Hamiltonian and overlap matrices) is 13. For odd parity states ($m=\pm 1$) ten basis functions are used.

The binding energy of the ground state ($1s$), E_{1s} , is then given by

$$E_{1s} = E_1 + \gamma - E, \quad (12)$$

where E_1 is the lowest subband energy of the square-well potential, γ is the energy of the first Landau level,¹⁰ and E is the eigenvalue of the Hamiltonian [Eq. (4)] corresponding to the $1s$ level, which has been determined variationally. The value of E_1 is determined by numerically solving the following transcendental equation:¹²

$$\left(\frac{E_1}{V_0} \right)^{1/2} = \cos[(E_1)^{1/2}L/2]. \quad (13)$$

The binding energies of the $2p_{\pm}$ states are obtained in a similar fashion. This procedure results in our variational binding energies being rigorous lower bounds for the true binding energies.

RESULTS AND DISCUSSION

Before we discuss the main results of our calculations, we would like to mention that for the case of the donor at the center of the well we have examined the importance of

using different effective masses for GaAs and $\text{Ga}_{1-x}\text{Al}_x\text{As}$ in our calculations of the donor energy levels in the presence of a magnetic field. Two separate sets of calculations of the binding energies of the ground and excited states with the impurity ion located at the center of the well were performed. One set of calculations used the GaAs value for the electron effective mass in both the barrier and the well materials. The interface matching conditions then required continuity of $f(z)$ of Eq. (8) and $\partial f/\partial z$ across the interface. These are the conditions used in our earlier work.⁵ The other set of calculations used the following expression for the effective mass in $\text{Ga}_{1-x}\text{Al}_x\text{As}$:

$$m^*/m_e = 0.067 + 0.083x. \quad (14)$$

The matching conditions used in this case were that $f(z)$ and $(m^*/m_e^*)\partial f/\partial z$ are continuous at the interface. These conditions are similar to those used by Mailhiot *et al.*⁴ and have been approximately justified for GaAs/ $\text{Ga}_{1-x}\text{Al}_x\text{As}$ interface, especially for small x , by the calculations of Ando and Mori.¹³ The differences between the values of the binding energies obtained in the two sets of calculations are small for $L \geq 25$ Å. In most cases they differ by less than a few percent; the binding energies obtained with different masses are somewhat larger. We have used two x values ($x=0.15$ and 0.3) and various values of γ and L . The largest difference between the two sets occurs for $x=0.15$, $L=25$ Å with small values of γ . They differ there by about 10% for both the ground and the excited states at zero magnetic field. It appears that, as far as the binding energies are concerned, it does not matter much which matching conditions are used, except for very small well widths. These conclusions, of course, apply only to the case of the donor at or near the center of the well.

The results presented in this section are obtained using different values of the effective mass in the two materials. We have used the same values of the dielectric constant in both materials, as for small x these values do not differ significantly. It should be pointed out that the matching conditions we have used are approximate. The accurate expressions of the matching conditions, which are valid at a given interface between two different semiconductors, have not yet been established.

In Figs. 1 and 2 we display the variation of the binding energy of the ground state (E_{1s}) and of the $2p_{-}$ state ($E_{2p_{-}}$) as a function of L for a few selected values of γ . For a given value of x , L , and γ , the energy of the $2p_{+}$ level, $E_{2p_{+}}$, is obtained from $E_{2p_{-}}$ by adding 2γ . The two figures illustrate the case of the donor at the center and edge of the well for a commonly used value of Al concentration $x=0.3$. For comparison, we also show the variation of E_{1s} and $E_{2p_{-}}$ with L for zero magnetic field. We first consider the on-center case, Fig. 1. As expected, the presence of a magnetic field leads to more binding. For the donor at the center of the well and a given value of x , the binding energies increase as L is reduced until they reach a maximum value, and then drop to a value characteristic of bulk $\text{Ga}_{1-x}\text{Al}_x\text{As}$ at $L=0$. The critical

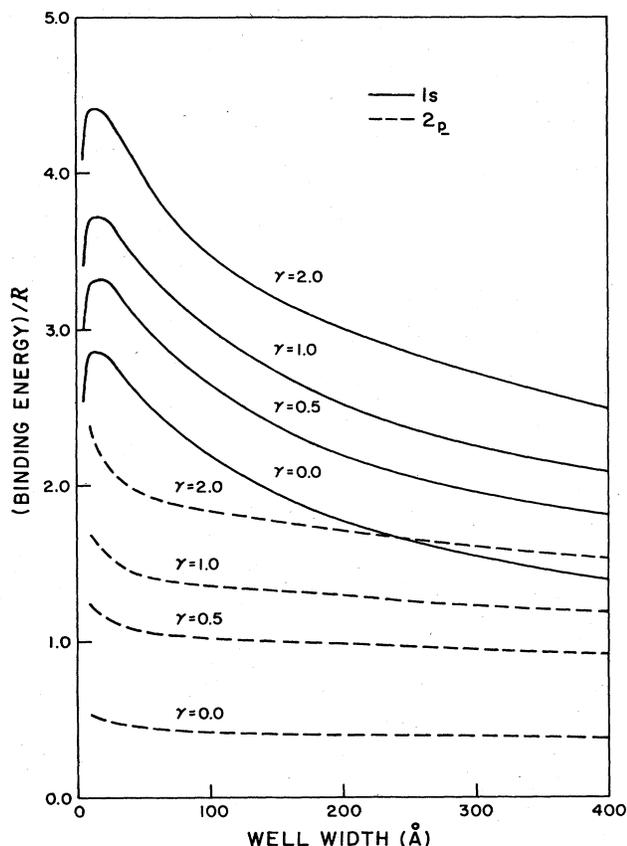


FIG. 1. Variation of the binding energy of the ground state and $2p_-$ excited state for a donor at the center of a GaAs quantum well as a function of the well size (L). Four different values of the magnetic field parameter γ ($=e\hbar B/2m^*cR$, as defined in the text) are shown. The Al concentration $x=0.3$. All energies are expressed in terms of an effective rydberg R^* ($=5.83$ meV).

well size L_c at which the maximum in E_{1s} is reached falls between 15–25 Å for $x=0.15$ (not shown) for values of γ considered in this work ($\gamma \leq 5$). For $x=0.3$, L_c is less than 10 Å. The energy of the $2p_-$ state peaks at even smaller values of L . The occurrence of the peaks at such small values of L is a result of using different effective masses in the GaAs and $\text{Ga}_{1-x}\text{Al}_x\text{As}$ materials. If the GaAs electron effective mass is used for both (as in our previous work), the peaks occur at about 25 Å.

The qualitative behavior of E_{1s} and E_{2p_-} with L is essentially similar and is easy to understand. As the value of L is reduced, the wave function becomes more compressed in the GaAs well, thus leading to more binding. However, beyond a certain value of L , which is different for different values of x , more and more of the wave function is found in surrounding $\text{Ga}_{1-x}\text{Al}_x\text{As}$, reducing the value of the binding energy. At $L=0$ the donor wave function is entirely in $\text{Ga}_{1-x}\text{Al}_x\text{As}$, leading to values which are characteristic of bulk $\text{Ga}_{1-x}\text{Al}_x\text{As}$. For a given state and value of x , the value of L_c is about the same for all values of the magnetic field. This is due to the fact that the portion of the wave function in

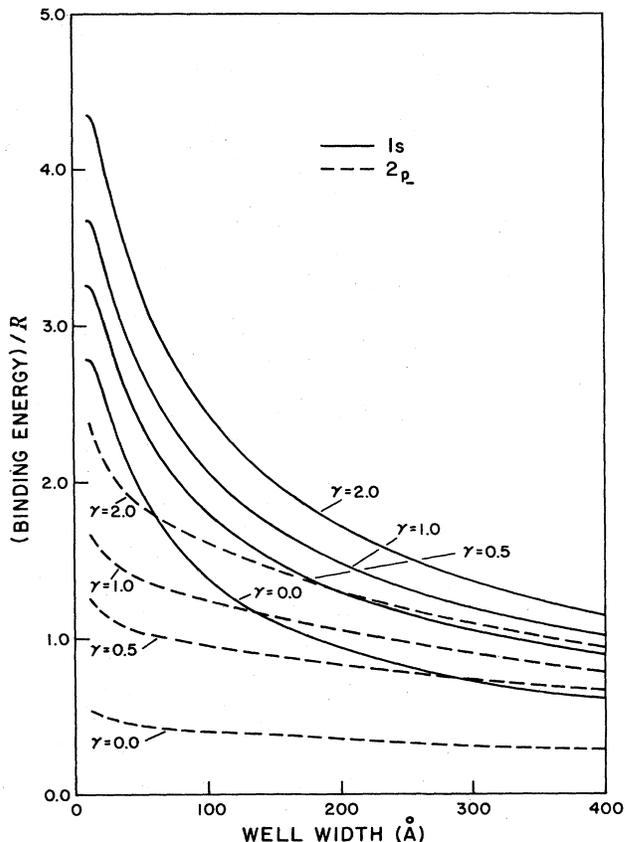


FIG. 2. Variation of the binding energy of the ground state and $2p_-$ excited state for a donor at an edge of a GaAs quantum well as a function of the well size (L). Four different values of the magnetic field parameter γ ($=e\hbar B/2m^*cR$, as defined in the text) are shown. The Al concentration $x=0.3$. All energies are expressed in terms of an effective rydberg R ($=5.83$ meV).

$\text{Ga}_{1-x}\text{Al}_x\text{As}$ is determined primarily by the function $f(z)$ which is independent of the magnetic field.

Careful examination of Fig. 1 will reveal that the separation between curves of different values of γ increases as L decreases. The effect is most clearly seen in the dashed, $2p_-$ curves. This is due to the fact that at smaller well widths the extension of the wave function in the x - y plane is reduced. This decreases the contribution of the magnetic term of the Hamiltonian [Eq. (4)] which is proportional to ρ^2 . A reduction of this positive term leads to an increase in the binding energy.

The behavior of binding energies in the case of the donor at an edge of the well, shown in Fig. 2, is similar. For small L the energies are slightly less than for the on-center case. However, they decrease more sharply as L is increased than do the corresponding on-center states. The reason for this is that the donor on-edge and on-center cases have distinctly different $L \rightarrow \infty$ limits. In the case of the donor at the center of an infinitely-wide, infinitely-high quantum well, the states that we have considered become hydrogenic $1s$ and $2p_-$ states. If the donor is at an edge of such a well, however, the states are mathematical-

ly equivalent to semi-infinite hydrogenic $2p_0$ and $3d_{\pm 10}$ states.

In Fig. 3 we show the dependence of the $1s$ to $2p_-$ transition energy upon the magnetic field for several values of L , again for Al concentration $x=0.3$. For a given value of L , the energy difference is only weakly dependent upon the magnetic field over the range of γ studied. The difference is, however, very dependent upon the well size, as could be seen in Figs. 1 and 2 as well. The curves of Fig. 3 dip for small values of γ because the magnetic field causes the electron wave function to shrink in the ρ direction. This initially affects the $2p_-$ state more strongly than the $1s$ state, due to its larger effective radius. As L is decreased, the minimum in the energy difference curves shifts to larger γ values. This is due to the fact that decreasing the size of the quantum well causes the extent of the wave function in the x - y plane (measured, for example, by $\langle \rho^2 \rangle$) to shrink relatively more for the ground state than for the excited state.

As noted earlier, we assumed the conduction-band discontinuity to be 85% of the total band-gap difference. It has been recently suggested that 50% may be a more appropriate value.¹⁴ For a given value of x the binding energies are found to be relatively insensitive to this suggested change in the barrier height.

Experimental data on the energy levels of donors in the presence of a magnetic field in quantum-well structures are rather limited at this time. Recently, Jarosik *et al.*¹⁵ have observed broad absorption lines that appear to be $1s \rightarrow 2p_-$ and $1s \rightarrow 2p_+$ transitions of the on-center hydrogenic donors in GaAs/Ga_{0.75}Al_{0.25}As quantum-well structures in a magnetic field. They have studied these transitions as a function of the magnetic field and of the well size. Their data are in good agreement with our calculations.

During the past three decades a great deal of effort has been devoted to the study of the behavior of energy levels of shallow donors and acceptors in semiconductors, both in the absence and in the presence of a magnetic field, using optical techniques such as far-infrared and photoluminescence spectroscopies. This study has provided a great deal of information concerning the nature of impurity states as well as the physical parameters of the semiconductors in which these impurities are imbedded. A similar detailed study of shallow impurities in quantum-well structures, we believe, will provide useful information about their energy levels as well as the properties of the quantum-well structures themselves.

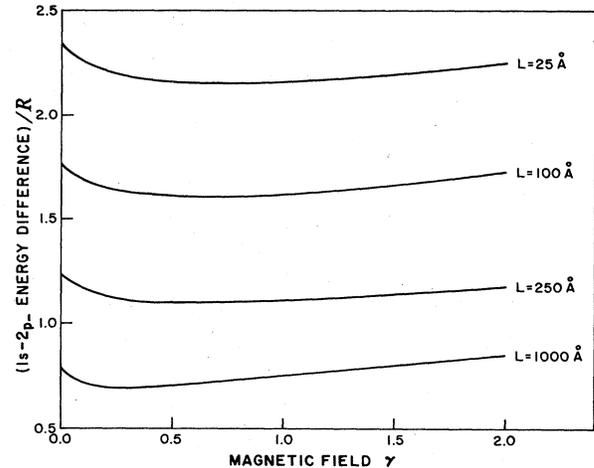


FIG. 3. Variation of the difference in energy between the ground state and $2p_-$ excited state as a function of the magnetic field parameter γ ($= e\hbar B/2m^*cR$, as defined in the text). The donor is at the center of the well. Four different GaAs well widths are shown. The Al concentration $x=0.3$, and the unit of energy is the GaAs effective rydberg R ($=5.83$ meV).

CONCLUDING REMARKS

We have calculated the binding energies of the ground state ($1s$) and of two excited states ($2p_{\pm}$) of a hydrogenic donor in a GaAs quantum well as a function of the potential-barrier height and the size of the quantum well in the presence of a magnetic field. We have considered the positively charged impurity ion to be located at the center or at the edge of the well. In addition, we assumed the applied magnetic field to be parallel to the axis of growth of the quantum-well structure. The trial variational wave functions were expressed in terms of Gaussian basis sets. As expected, we found that for a given value of the magnetic field, the binding energies are larger than their values in a zero magnetic field. For a given magnetic field, the change in the binding energy due to the magnetic field increases slowly as the well size is reduced. This is true for both the ground state and the excited states.

ACKNOWLEDGMENTS

The research of one of us (R.L.G.) was sponsored by the Air Force Office of Scientific Research, Air Force Systems Command, U. S. Department of the Air Force, under Grant No. AFOSR-83-0120.

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