Energy spectra of donors in GaAs–Ga$_{1-x}$Al$_x$As quantum well structures in the effective mass approximation

C. Mailhiot, Yia-Chung Chang,[a] and T. C. McGill

California Institute of Technology, Pasadena, California 91125

We present the results of a study of the energy spectrum of the ground state for shallow donors in quantum well structures, consisting of a single slab of GaAs sandwiched between two semi-infinite layers of Ga$_{1-x}$Al$_x$As. The effect of the position of the impurity atom within the central GaAs slab is investigated for different slab thicknesses and alloy compositions. Two limiting cases are presented: One in which the impurity atom is located at the center of the quantum well (on-center impurity), the other in which the impurity atom is located at the edge of the quantum well (on-edge impurity). Both the on-center and the on-edge donor ground state are bound for all values of GaAs slab thicknesses and alloy compositions. The alloy composition x is varied between 0.1 and 0.4. In this composition range, Ga$_{1-x}$Al$_x$As is direct and the single-valley effective mass theory is a valid technique for treating shallow donor states. Calculations are carried out in the case of finite potential barriers determined by realistic conduction band offsets.

I. INTRODUCTION

The unique nature of electronic states associated with semiconductor superlattices has been the subject of a great deal of interest both from the theoretical[1–6] and experimental[7–10] viewpoints. In view of the potential applications of these structures,[11–14] the understanding of impurity states found within these systems is an issue of technical as well as scientific importance.

In this paper, we report on a study of the energy spectrum of shallow donor states in a single GaAs–Ga$_{1-x}$Al$_x$As quantum well, i.e., a structure formed by a central GaAs slab (well material) flanked by two semi-infinite Ga$_{1-x}$Al$_x$As layers (barrier material). The energy spectrum of a donor state located within the GaAs slab is studied as a function of the width of the rectangular potential well formed by the conduction band offset at the GaAs–Ga$_{1-x}$Al$_x$As interface. The effect of the alloy composition x in the barrier material, as well as the position of the donor atom within the well, are also investigated. Two positions of the donor were studied: (1) donor ion at the center of the quantum well (on-center impurity) and (2) donor ion on the edge of the quantum well boundary (on-edge impurity). We find that the donor energy spectrum, both for the on-center and the on-edge impurity, is considerably modified as the dimension of the quantum well is varied. Both the on-center and the on-edge donor energies, with respect to the first conduction subband versus GaAs slab thickness, present a maximum (in absolute value) whose magnitude depends on the alloy composition. The on-edge impurity, produces a more shallow donor ground state than the on-center impurity. This reduction of binding of the on-edge donor ground state results from the fact that the repulsive barrier potential tends to push the electronic charge distribution away from the attractive ionized center, thereby leading to a reduced effective Coulomb attraction. This finding is in accord with previous calculations carried out in the case of infinite confining potential.[15]

In Sec. II, we present the calculation techniques. We discuss first the effective mass Hamiltonian used for treating the shallow states and its validity, then we describe the basis orbitals on which the donor state is expanded. In Sec. III, the main results are presented. First, we discuss the energy spectrum for the on-center impurity, then we treat the case of the on-edge impurity. A comparison is made between these two limiting cases. A summary of the results and a conclusion are presented in Sec. IV.

II. CALCULATIONAL METHOD

Calculations are based on the effective mass approximation (EMA). The GaAs–Ga$_{1-x}$Al$_x$As system was chosen since the EMA is known to hold to a high degree of accuracy for shallow donor states in GaAs.[16] As shown by Ando and Mori,[17] the boundary conditions that the donor envelope function and the particle current are continuous across the interface are adequate in the case of GaAs–Ga$_{1-x}$Al$_x$As quantum well structures.

The composition of the Ga$_{1-x}$Al$_x$As alloy was varied in the range where the alloy remains direct, so that the single-valley effective mass theory still holds. Realistic conduction band offsets of finite magnitude were used, thereby allowing the wave function to penetrate into the barrier material as the dimensions of the confining quantum well are reduced. The use of finite conduction band offsets has a large effect on the binding energy of the donor state in the thin GaAs slab limit and should be compared with approximate calculations carried out using infinitely high barrier height (quantum box),[18,19] in which case the donor wave function is required to vanish at the interface. When finite conduction band offsets are taken into account, the condition that the wave function vanishes at the interface is relaxed and penetration in the barrier material is allowed. The infinite barrier case should be viewed as a limiting case valid only for very
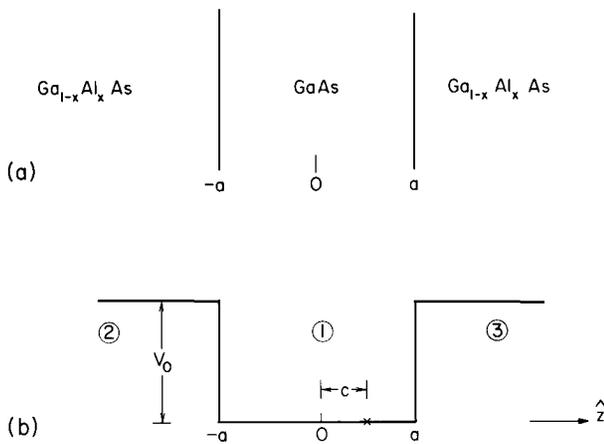
FIG. 1. Geometry of a Coulomb center located at a distance c from the center of a finite quantum well of width $2a$ (along the $\hat{z}$ direction) and height V_0. (a) physical structure; (b) quantum well potential profile along the $\hat{z}$ axis normal to the interfaces.

wide quantum wells for which the penetration of the donor state into the barrier material is small.

The effective mass Hamiltonian corresponding to a Coulomb center located at a distance c from the center of a finite quantum well of width $2a$ along the $\hat{z}$ direction (the $\hat{z}$ axis is normal to the interface plane) and height V_0 (see Fig. 1 for geometry) is

$$\widehat{H}(1) = \frac{-\hbar^2}{2m_1^*}\nabla^2 + V_1(\mathbf{r}), \quad \text{in region (1)}, \tag{1a}$$

$$\widehat{H}(2) = \frac{-\hbar^2}{2m_2^*}\nabla^2 + V_2(\mathbf{r}) + V_0, \quad \text{in region (2)}, \tag{1b}$$

$$\widehat{H}(3) = \frac{-\hbar^2}{2m_2^*}\nabla^2 + V_3(\mathbf{r}) + V_0, \quad \text{in region (3)}, \tag{1c}$$

where m_1^* refers to the bulk GaAs (well material) effective mass and m_2^* refers to the interpolated effective mass in $Ga_{1-x}Al_xAs$ (barrier material). The origin of the coordinates is taken on the ionized donor. Since the bulk dielectric constants of GaAs and $Ga_{1-x}Al_xAs$, ϵ_1 and ϵ_2, respectively, differ slightly, the Hamiltonian must include terms due to electrostatic image charges.[20,21] The potentials $V_1(\mathbf{r})$, $V_2(\mathbf{r})$, and $V_3(\mathbf{r})$ represent the Coulomb interaction between the electron and the impurity ion as well as the ion image charge. The expressions for the electron–ion potential $[V_i(\mathbf{r})]$ will be given elsewhere.[22]

The conduction band offset V_0 was taken to be 85% of the difference of the $\mathbf{k} = 0$ band gaps of GaAs and $Ga_{1-x}Al_xAs$.[23] Since the alloy composition range studied was such that the alloy was direct $(x < 0.45)$,[23] both the effective mass m_2^* and the conduction band offset V_0 were determined using the $\mathbf{k} = 0$ values of $Ga_{1-x}Al_xAs$[23]

$$m_1^* = 0.067\, m_0, \tag{2a}$$

$$m_2^* = (0.067 + 0.083x)m_0, \tag{2b}$$

$$\epsilon_1 = 13.1\epsilon_0, \tag{2c}$$

$$\epsilon_2 = [13.1(1 - x) + 10.1x]\epsilon_0, \tag{2d}$$

$$V_0 = 1.06x \text{ eV}, \tag{2e}$$

where m_0 and ϵ_0 are the free electron mass and the vacuum static dielectric constant, respectively.

To calculate energies with respect to the first conduction subband, we must solve for the Hamiltonian in Eqs. (1) without the impurity potentials $V_1(\mathbf{r})$, $V_2(\mathbf{r})$, and $V_3(\mathbf{r})$. Letting $\widehat{H}_0$ be the Hamiltonian without the impurity potential, the energies (E) of the Coulomb states with respect to the first conduction subband edge are given by the difference between the donor energy $E(\widehat{H})$, and the subband energy $E(\widehat{H}_0)$: $E = E(\widehat{H}) - E(\widehat{H}_0)$.

Calculations were carried out using a variational method. To preserve the cylindrical geometry of the system, the trial basis orbitals on which the donor state envelope function is expanded is of the form of Gaussian-type orbitals (GTO's), defined in an ellipsoidal coordinate system and shifted with respect to the ionized donor taken to be at the origin

$$\langle \mathbf{r}'|nlm\rangle \equiv \phi_{nlm}(\mathbf{r}') = \sum_{i=1,2,3} N_i(n,l)[r(\lambda,d_i)']^l$$

$$\exp\{-\zeta_i(n,l)[r(\lambda,d_i)']^2]\}Y_l^m(\Omega'), \tag{3}$$

where $r(\lambda,d_i)' \equiv [x^2 + y^2 + \lambda^2(z - d_i)^2]^{1/2}$, and $N_i(n,l)$ is a normalization constant. The index $i = 1,2,3$ labels the region of space where the GTO orbital is defined. The boundary conditions that both the wave function and the particle current are continuous across the interface[24] determine relations between the normalization constants $N_i(n,l)$ and the orbital exponents $\zeta_i(n,l)$ in the barrier material $(i = 2,3)$ in terms of those in the well material $(i = 1)$. To produce an accurate description of the donor envelope wave function, a shape parameter (λ), as well as a shift parameter (d_i), were incorporate in the variational basis set $\{|nlm\rangle\}$. The shape parameter λ determines the compression of the envelope function along the quantum well axis $(\hat{z})$. The shift parameter d_i determines the location of the electron charge distribution when the impurity ion is moved towards the quantum well edge. In the calculation presented here, we chose: (1) $d_i \equiv 0$ in the case of the on-center impurity and (2) $d_0 \neq 0$ for $l = 0$ and $d_l = 0$ for $l \neq 0$ in the case of the on-edge impurity. The GTO orbital exponents $\zeta_1(n,l)$ appearing in the Eq. (3) are fixed and taken to be of the form (in atomic Rydberg units[25]) $\zeta_1(n,l) = \zeta_0/b(n)(l + 1)$, with $b(n) = \{1,2,4,8,16,32,1/2\}$ and $\zeta_0 = 8/(9\pi)$ bohr^{-2}. The donor envelope function $|\Psi\rangle$ is expanded on the set of basis orbitals $\{|nlm\rangle\}$ defined in Eq. (3). We then solve the EMA Schrödinger equation for the donor envelope function

$$\widehat{H}|\Psi\rangle = E(\widehat{H})|\Psi\rangle, \tag{4}$$

for the eigenenergy $E(\widehat{H})$.

Calculations were carried out using seven s-like $(l = 0)$ and seven p-like $(l = 1)$ GTO's. In the case of the on-center impurity $(c = 0)$, the Hamiltonian in Eqs. (1) mixes only orbitals whose angular momentum l differ by an even integer. For the on-center impurity, only s-like GTO's were included in the expansion of the donor wave function. However, for the on-edge impurity $(c = a)$, the mixing between s- and p-like orbitals becomes appreciable and must be included to provide an accurate description of the neutral donor. The calculation of the subband energy $E(\widehat{H}_0)$ was carried through using only s-like GTO's. For each value of GaAs slab thickness

(2a), impurity position (c), and barrier height V_0, the shape parameter λ, as well as the shift parameter d_I were determined by minimizing the energy expectation value in the ground state $E_0(\lambda, d_I)$.

This shifted ellipsoidal Gaussian set has the advantage of reproducing reasonably well the Coulomb center at both the small $(a \rightarrow 0)$ and the large $(a \rightarrow \infty)$ slab thickness limit where the binding energy reduces, in the case of the on-center donor, to that of the barrier material or the well material bulk values, respectively. At the same time, it retains the nonspherical character of the problem and allows the basis orbitals to reshape themselves in order to minimize the total energy. The inclusion of a shift parameter d_I in the variational basis set allows the electronic charge distribution associated with the donor ground state envelope function to be shifted away from the position of the impurity ion. This degree of freedom appears to be most important in the case of the on-edge donor where the Coulomb potential tends to pull the charge distribution towards the ionized center, whereas the repulsive barrier potential tends to push it away from the ionized center.

III. RESULTS

We first treat the results obtained for the on-center impurity case $(c = 0)$. Then we treat the on-edge impurity case $(c = a)$. Comparisons are made between these two limiting cases for the donor ground state.

Figure 2 shows the energy, with respect to the first conduction subband, for the on-center donor ground state as a function of GaAs slab thickness for four alloy compositions $x = 0.1, 0.2, 0.3, 0.4$. For the on-center impurity, the energy with respect to the first conduction subband versus GaAs slab thickness presents a maximum (in absolute value) whose magnitude depends on the alloy composition of the barrier material. Greater Al composition in the barrier material leads to larger conduction band offsets and therefore more complete confinement of the donor envelope function. Since greater confinement of the donor state leads to a more sharply peaked wave function as the envelope function builds up amplitude around the impurity ion, the attractive Coulomb potential is more effective in binding the donor state when the Al content in the $Ga_{1-x}Al_xAs$ barrier is increased. For large GaAs slab thicknesses, the effect of the alloy composition x or, equivalently, of the barrier height V_0, on the on-center donor ground state energy and wave function is greatly reduced since the envelope function is strongly localized around the impurity ion in the center of the quantum well and does not feel much the repulsive barrier potential.

Figure 3 shows the energy, with respect to the first conduction subband, of the on-edge donor ground state as a function of the GaAs slab thickness for four alloy compositions $x = 0.1, 0.2, 0.3, 0.4$. The on-edge donor energy curve presents qualitatively the same features as the on-center donor energy curve. In the thin GaAs slab limit, the energy curves for the on-center and the on-edge donor are very similar. In the thick GaAs slab limit, the on-edge donor is less tightly bound than the on-center donor. This is mainly due to the fact that, as the impurity ion approaches the quantum
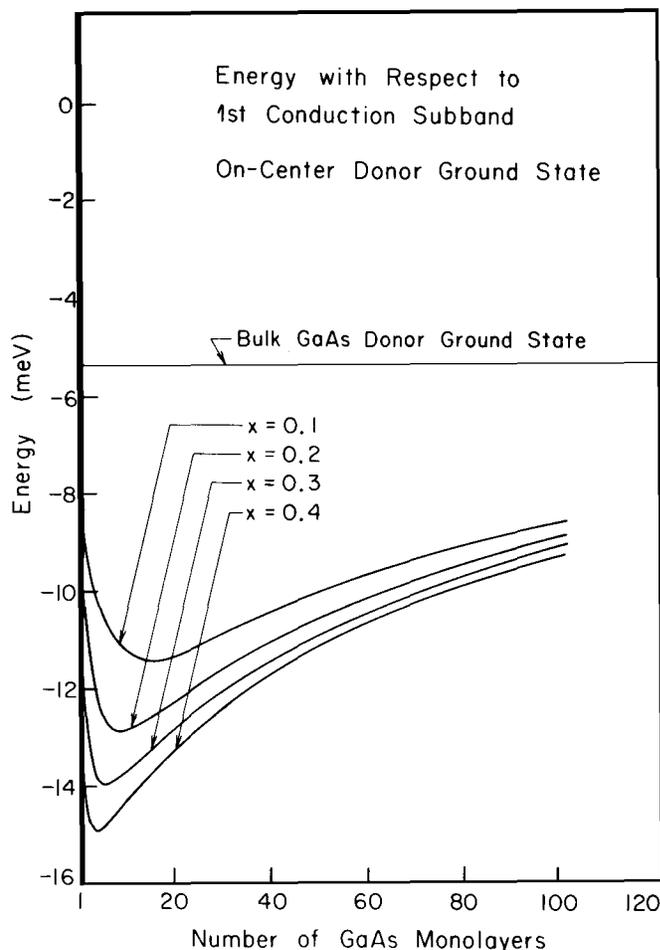

FIG. 2. Energy of the on-center donor ground state with respect to the first conduction subband as a function of GaAs slab thickness for four alloy compositions $x = 0.1, 0.2, 0.3, 0.4$, of $Ga_{1-x}Al_xAs$. Calculations are carried through using seven *s*-like ellipsoidal Gaussian-type orbitals, as defined in the text.

well edge, the donor ground state envelope function should be constructed more and more from Bloch states derived from the $Ga_{1-x}Al_xAs$ conduction band edge. These states lie above the GaAs conduction band edge by an energy equal to the conduction band offset between GaAs and $Ga_{1-x}Al_xAs$. As the on-edge donor ground state envelope function includes more of these higher energy states, the on-edge donor ground state becomes more shallow than the on-center donor ground state. Furthermore, in the case of the on-edge center, the repulsive barrier potential tends to push the electronic charge distribution away from the ionized donor, leading to a reduced Coulomb attraction. For the on-edge impurity, the results presented here using finite conduction band offsets are qualitatively similar to the case where infinite band offsets are assumed,[15] thereby preventing the donor envelope function from leaking out of the quantum well. The dashed line in Fig. 3 indicates the energy with respect to the first conduction subband in the limit of large GaAs slab. The boundary conditions on the wave function at the interface for the finite conduction band offset case gives the donor envelope function a d-like character as the slope of the wave function is vanishingly small on the donor center. In the large slab limit, the p-like character of the
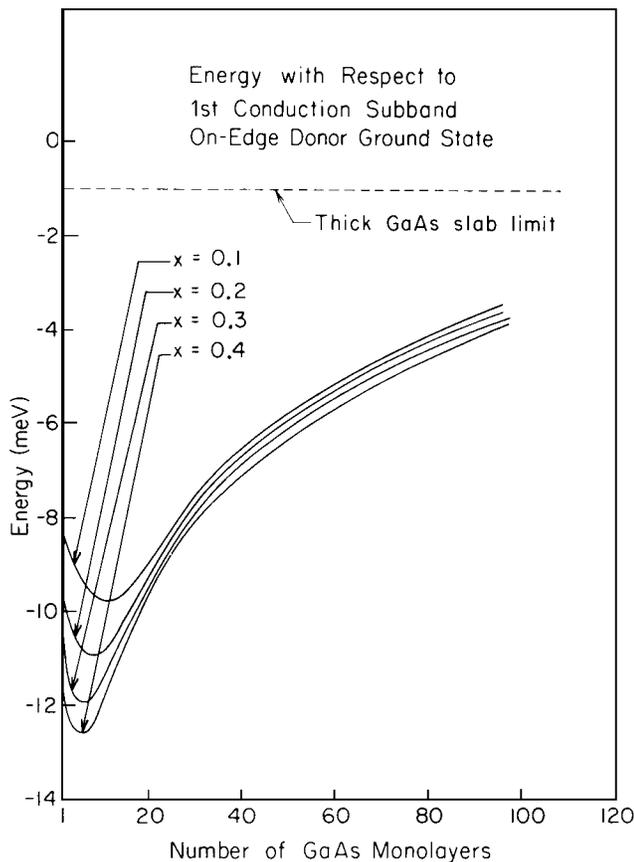
FIG. 3. Energy of the on-edge donor ground state with respect to the first conduction subband as a function of GaAs slab thickness for four alloy compositions $x = 0.1, 0.2, 0.3, 0.4$, of $Ga_{1-x}Al_x As$. Calculations are carried through using seven s-like and seven p-like ellipsoidal Gaussian-type orbitals, as defined in the text. The dashed line indicates the energy with respect to the first conduction subband in the large GaAs slab thickness limit.

donor envelope function is less important and the donor ground state mostly consists of shifted s-like orbitals.

IV. SUMMARY AND CONCLUSION

We have calculated the energy spectrum of shallow donor states in $GaAs-Ga_{1-x}Al_x As$ quantum well structures using the effective mass approximation scheme. The variation in energy with respect to the first conduction subband of the donor ground state was studied as a function of the central GaAs slab thickness, the position of the impurity atom within the GaAs slab and the alloy composition x of $Ga_{1-x}Al_x As$. Calculations were done for four alloy compositions of $Ga_{1-x}Al_x As$ in a range in which the alloy remains direct ($x < 0.45$). Realistic values for conduction band offsets of finite magnitude were used. The effect of the impurity position on the binding energy of the donor state was investigated in the two limit cases where the impurity ion was at the center of the quantum well (on-center impurity) and at the edge of the quantum well (on-edge impurity).

In the case of both the on-center and the on-edge impurities, the energy with respect to the first conduction subband versus slab thickness presents a maximum (in absolute value) corresponding to a maximum confinement of the donor state envelope wave function. In the case of the on-edge impurity,

the donor ground state is not as tightly bound as the on-center ground state. The reduction in the binding for the on-edge impurity is a direct consequence of the repulsive interface potential which tends to push the electronic charge distribution away from the Coulomb center.

For both the on-center and the on-edge impurity, it was found that the energy spectrum of the donor ground state is considerably modified as the thickness of the GaAs slab containing the impurity was varied. This variation in binding energy should be easily observed experimentally, since molecular-beam epitaxy (MBE) techniques[26] now allow for the fabrication of superlattices consisting of alternating slabs of few monolayers of $GaAs-Ga_{1-x}Al_x As$. It seems possible to adjust the binding of a Coulomb center in a superlattice by varying the thickness of the slab containing the impurity center.

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a) Present address: Department of Physics, University of Illinois, Urbana, Illinois 61801.

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