Shallow donor impurities in GaAs-$Ga_{1-x}Al_xAs$ quantum-well structures: Role of the dielectric-constant mismatch

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We present a variational method to compute donor eigenstates in a GaAs-$Ga_{1-x}Al_xAs$ quantum well. The effective-mass approximation is used, and the envelope function is expanded in the complete set of the states of the quantum well at $\mathbf{k}_{\parallel}=\mathbf{0}$, including the continuum states. The convergence is good; the contribution of the continuum is very small, except for odd states in narrow wells, where there are no bound subband states of the required symmetry in the quantum well. The results obtained for all impurity positions and for various values of the well thickness show a much larger effect of the dielectric-constant mismatch than previously anticipated, such effect being larger for off-center impurity positions. The far-infrared absorption coefficient is computed for both polarizations of the radiation, with the spatial impurity distribution taken into account. Good agreement is found with available experimental data.

I. INTRODUCTION

In the last decade semiconductor heterostructures have received a great deal of attention because of their intrinsic physical interest and their technological applications in electronic devices. The most often employed semiconductors are of the III-V compound type, as in the GaAs-$Ga_{1-x}Al_xAs$ system, which is the most thoroughly studied and the one of the greatest technological promise. In a GaAs-$Ga_{1-x}Al_xAs$ quantum well (QW) the difference in the band gap of the two semiconductors acts as an additional square-well potential which confines the carriers (both electrons and holes) in the inside layer. Many physical properties of the carriers depend strongly on spatial confinement; in the limit of narrow QW's, carriers behave very much as a two-dimensional (2D) electron (or hole) gas. A good example of the transition between a 3D-like character of the electronic properties and a 2D-like one, depending on the thickness of the well, is given by the states of shallow impurities. This problem has been studied by means of the effective-mass (EM) approximation by a large number of authors: among others Bastard,[1] Mailhiot *et al.*,[2,3] Priester, *et al.*,[4] Greene and Bajaj,[5] Lane and Greene[6] and Chang[7] for the donor states, and Masselink *et al.*[8] for the acceptor states. The extension of the EM approximation to heterostructures requires appropriate boundary conditions at the interfaces;[9] these involve only the envelope functions provided that constituent materials are chemically similar, as in the GaAs-$Ga_{1-x}Al_xAs$ system.

The purpose of this paper is to study the far-infrared absorption in an isolated GaAs-$Ga_{1-x}Al_xAs$ QW doped with shallow donor impurities in the central layer. The wave functions and the eigenvalues of the donor states are obtained by solving the EM equation by means of the variational method; there is no analytical solution in closed form of this equation because of the simultaneous presence of two potentials with different symmetries: the spherically symmetric Coulomb potential and the square-well potential. We propose a variational treatment similar to that of Ref. 3, based on expanding the impurity eigenfunctions in the eigenstates of the QW without impurities at $\mathbf{k}_{\parallel}=\mathbf{0}$. We also include the continuum states of the QW in order to verify the convergence on a complete basis set. This is done by means of a large box surrounding the system, which causes all the states to be discrete. Part of these states (say up to an energy Λ_{max}) are explicitly considered in the Hamiltonian matrix, whereas the other states (with energy higher than Λ_{max}) are treated in second-order perturbation theory to test the convergence of the results and to give an estimate of the error. Our method is very consistent to treat narrow and moderately large QW's, but we have also verified the 3D limit: the bulk donor spectrum is achieved with high accuracy for very large QW's.

A distinct advantage of our method is the exact treatment of the difference in the values of the dielectric constants in the two materials. In most of the previous papers this effect was neglected on the assumption of its irrelevance. Where comparisons were made different expansion sets were considered, so that a real assessment of the role of the dielectric-constant mismatch is not available. We find that this effect is considerable, and it increases with decreasing the well width and displacing the impurity to off-center positions (a typical value of 10% of the binding energy is obtained).

The simplicity of the method allows extensions to more complicated cases. We are presently studying the problem of shallow donors in a magnetic field along the QW axis and that of shallow acceptors (including the mixing

of heavy and light holes); moreover, we belive that the method could be applied to the problem of excitons in QW's.

The remaining part of this paper is organized as follows. In Sec. II we present our approach to the problem of shallow donor impurities in a QW (the treatment of the continuum states by second-order perturbation theory is described in the Appendix). In Sec. III we present results for both ground and excited states; we also compare our results with those of previous theoretical analyses. In Sec. IV we compute the ir absorption for various impurity distributions, for both polarizations of the incident radiation [parallel ($\|$) and perpendicular ($\perp$) to the QW axis], and compare the results with currently available experimental data. Section V is devoted to the conclusions.

II. METHOD OF CALCULATION

The system we consider is a single QW grown in the [001] direction, which we take as the quantization axis, and with composition $x < 0.43$,[10] such that both the well and the barrier materials have a direct gap at the Γ point of the Brillouin zone. The well extends from $-L/2$ to $L/2$. If the doping density is not too high we can consider an isolated impurity, located at the point z_0 inside the well.

We describe the system by means of the EM Hamiltonian

$$H=\frac{\hbar^2\mathbf{k}^2}{2m^*}+V_{\mathrm{QW}}(z)+V_{\mathrm{imp}}(\mathbf{r}) , \tag{1}$$

where $\mathbf{k}=-i\nabla$ and the effective mass m^* is that appropriate to the well (m_1^*) and to the barrier (m_2^*) material for $|z|<L/2$ and $|z|>L/2$, respectively. $V_{\mathrm{QW}}(z)$ is the square-well potential, which vanishes inside the well and equals V_0 in the barriers. The impurity potential V_{imp} is the screened Coulomb potential satisfying Maxwell boundary conditions at both interfaces. Summing a series of image charges we obtain

$$V_{\mathrm{imp}}(\mathbf{r})=\begin{cases} -\dfrac{(1+\beta)e^2}{\epsilon_1}\left[\dfrac{1}{R_0}+\displaystyle\sum_{n=1}^{\infty}\beta^n\frac{1}{R_n^+}\right] & \text{for } z<-L/2, \quad (2a)\\ -\dfrac{e^2}{\epsilon_1}\left[\dfrac{1}{R_0}+\displaystyle\sum_{n=1}^{\infty}\beta^n\left[\frac{1}{R_n^+}+\frac{1}{R_n^-}\right]\right] & \text{for } |z|<L/2 , \quad (2b)\\ -\dfrac{(1+\beta)e^2}{\epsilon_1}\left[\dfrac{1}{R_0}+\displaystyle\sum_{n=1}^{\infty}\beta^n\frac{1}{R_n^-}\right] & \text{for } z>L/2 , \quad (2c)\end{cases}$$

where $\beta=(\epsilon_1-\epsilon_2)/(\epsilon_1+\epsilon_2)$, ϵ_1 and ϵ_2 being the static dielectric constants inside and outside the well, respectively; $R_0=[\rho^2+(z-z_0)^2]^{1/2}$ and $R_n^{\pm}=[\rho^2+(z-z_n^{\pm})^2]^{1/2}$ are the distances from the image charges, located in the two barriers at

$$z_n^{\pm}=\begin{cases} z_0\pm nL & \text{for even } n , \quad (3a)\\ -z_0\pm nL & \text{for odd } n . \quad (3b)\end{cases}$$

The EM equation for the envelope function $F(\mathbf{r})$,

$$HF(\mathbf{r})=EF(\mathbf{r}) , \tag{4}$$

is explicitly obtained from Eqs. (1)–(3). The current-conserving boundary conditions for $F(\mathbf{r})$ at the interface between materials I and II, at $z=L/2$, are

$$F^{\mathrm{I}}(\mathbf{r})|_{z=L/2}=F^{\mathrm{II}}(\mathbf{r})|_{z=L/2} , \tag{5}$$

$$\frac{1}{m_I^*}\frac{\partial F^{\mathrm{I}}(\mathbf{r})}{\partial z}\bigg|_{z=L/2}=\frac{1}{m_{\mathrm{II}}^*}\frac{\partial F^{\mathrm{II}}(\mathbf{r})}{\partial z}\bigg|_{z=L/2} ;$$

the corresponding conditions are imposed also at the other interface at $z=-L/2$. Conditions (5) are equivalent to the usual boundary conditions for the wave function only if the Bloch functions of the conduction band at the point $\mathbf{k}=\mathbf{0}$ are taken to be equal in both materials:[9]

$$u_{c0}^{\mathrm{I}}(\mathbf{r})\simeq u_{c0}^{\mathrm{II}}(\mathbf{r}) , \tag{6}$$

a condition which is well satisfied in the system we are presently considering.

In our formalism we do not include the effect of the nonparabolicity of the conduction band in bulk GaAs. This effect has been considered in the donor problem by Chaudhuri and Bajaj[11] by means of an energy-dependent isotropic effective mass. A more refined treatment of the conduction-band dispersion in bulk GaAs and in a QW has also been considered,[12,13] including cubic anisotropy. Using the band parameters given in Refs. 12 and 13, we have estimated the correction to the binding energy of a donor in a QW; we find an increase in the binding energy by less than 4% for $L>100$ Å, and by about 8% for $L=50$ Å. The same type of estimate would be meaningless for smaller values of L, because the fitting procedure which gives the band parameters in GaAs loses its validity and nonparabolicity effects in the barriers should also be considered. In this paper we choose to concentrate on a method for solving the donor problem and will stress the importance of considering the different effective masses and dielectric constants in the two materials.

Also neglected are the corrections to the binding energy of the donor states due to central cell effect, dynamical polaronic effect, and coupling between the Γ minimum of the conduction band and the secondary minima near the X points of the Brillouin zone: all these corrections are much smaller than the ones mentioned above.

Since the EM equation (4) with the boundary conditions (5) has no analytical solution, we adopt a variational

approach and must choose a convenient basis set for the linear expansion. Since the values of the well thickness we are interested in are of the same order of magnitude as the effective Bohr radius of a donor in bulk GaAs ($a^*=99$ Å), the separation in energy between the subbands of the QW is about 1 order of magnitude greater than the binding energy of a donor in the same system, as deduced from experimental as well as theoretical estimates. Therefore we find it convenient to expand the envelope function $F(\mathbf{r})$ of Eq. (4) in the eigenstates of the EM Hamiltonian of the impurity-free QW,

$$\psi_{n\mathbf{k}_\parallel}(\mathbf{r})=\exp(i\mathbf{k}_\parallel\cdot\mathbf{r}_\parallel)f_{n\mathbf{k}_\parallel}(z) \ . \tag{7}$$

The envelope function is then put in the form

$$F(\mathbf{r})=\sum_{n\mathbf{k}_\parallel} A_{n\mathbf{k}_\parallel}\psi_{n\mathbf{k}_\parallel}(\mathbf{r})=\sum_n g_n(\mathbf{r}_\parallel)f_{n,\mathbf{k}_\parallel=0}(z) \ , \tag{8}$$

where the completeness of the $\psi_{n\mathbf{k}_\parallel}$ at a fixed $\mathbf{k}_\parallel$ (in particular we have chosen $\mathbf{k}_\parallel=\mathbf{0}$) has been exploited: n runs over the discrete and the continuous spectrum, and the functions f_{n0} are those of the zone center QW states, and satisfy the boundary conditions (5). Axial symmetry requires us to choose the functions $g_n(\mathbf{r}_\parallel)$ in the form $e^{im\theta}\rho^{|m|}h_n(\rho)$, where m is the z component of the orbital angular momentum of the particular state considered. The whole problem is now reduced to the choice of a suitable expansion set for $h_n(\rho)$, which is well behaved and tends to a constant for $\rho\ll a^*$. Since, for $L\to 0$ and $V_0=\infty$, our problem reduces to the two-dimensional hydrogen problem, where the long-range behavior of h_n is $\exp(-\alpha\rho)$, we adopt, for any fixed value of m, the following expansion:

$$F(\mathbf{r})=\sum_{n,j} C_{nj}e^{im\theta}\rho^{|m|}e^{-\alpha_j\rho}f_{n0}(z) \ , \tag{9}$$

where the α_j are fixed *a priori* so as to cover the physical range, and the C_{nj} are treated as variational parameters, which are determined by solving the generalized eigenvalue problem

$$\langle nj|H|n'j'\rangle C_{n'j'}=E\langle nj|n'j'\rangle C_{n'j'} \ . \tag{10}$$

We remark that the boundary conditions (5) for $F(\mathbf{r})$ are automatically satisfied. The matrix elements appearing in Eq. (10) can easily be computed. The contributions from the kinetic and the square-well terms of H are straightforward, because the f_{n0} are eigenstates of the QW effective-mass equation without impurities. The contribution from the impurity potential may be reduced to a one-dimensional integral on an auxiliary variable s, by using in summations (2) the well-known transformation

$$\frac{1}{[\rho^2+(z-z_0)^2]^{1/2}}=\int_0^\infty e^{-|z-z_0|s}J_0(\rho s)ds \ , \tag{11}$$

in terms of the Bessel function J_0. This transformation allows us to perform analytically the sum of the image charges in Eq. (2) and the ρ and z integrals in the matrix elements of V_{imp}: only the integral in the auxiliary variable s is computed numerically.

To achieve convergence in expansion (9) no more than ten exponentials are required for the ground and excited states. The sum over the subband index n has a convergence rate which depends on the well thickness. In general the contribution of the continuum states must be considered, particularly in the case of narrow QW's, where there is only one electron bound state at $\mathbf{k}_\parallel=\mathbf{0}$, and therefore it would be impossible to discuss the convergence rate without considering the continuum states. They are properly introduced placing the QW in a large box ($V_{\text{box}}=0$ for $|z|<L_0/2$ and $V_{\text{box}}=\infty$ for $|z|>L_0/2$), which has the purpose of maintaining the discreteness of the basis set. The width L_0 is chosen sufficiently large to have a negligible ($<0.1\%$) effect on the binding energies of impurities. We have found that this is fully accomplished, for all the values of the well thickness considered here, by choosing $L_0\sim 8a^*$.

The lowest states of the continuum, say up to an energy $\Lambda_{\max}$, are included explicitly in the basis set, in order to improve the convergence of the results. The other states are used to give an estimate, by means of perturbation theory, of the error involved in truncating the sum over n, in expansion (9), at the energy $\Lambda_{\max}$. The details of the calculation are presented in the Appendix. For the ground state, for which the slowest convergence rate is expected, the correction to the binding energy caused by the states of the continuum with energy higher than $\Lambda_{\max}$ is estimated to be

$$\Delta E(\Lambda_{\max})\simeq\frac{1}{6\pi^3}\left[\frac{e^2\alpha}{\epsilon_1}\right]\left[\frac{e^2}{\epsilon_1 L}\right]\left[\frac{\hbar^2\alpha^2}{2m_1^*}\right]^{1/2}\left[\frac{2}{3}+\ln\left[\frac{\Lambda_{\max}}{\hbar^2\alpha^2/2m_1^*}\right]\right](\Lambda_{\max})^{-1.5} \ , \tag{12}$$

where α is a suitable average value of the exponents α_j used in Eq. (9). For $L\sim 50$ Å we estimate the relative correction to be $\Delta E(\Lambda_{\max})/E_0\simeq 0.1(\Lambda_{\max}/1\ \text{Ry}^*)^{-1.5}$, where 1 Ry$^*=5.8$ meV is the effective Rydberg in bulk GaAs. This correction decreases rapidly for increasing $\Lambda_{\max}$ and is found to be negligible for all the values of the well thickness considered here.

The total contribution of the states of the continuum, i.e., the states with energy greater than V_0, is very small (0.7% for the ground state, for $L=30$ Å) when at least one discrete bound state of the required symmetry under specular reflection $z\to -z$ exists at $\mathbf{k}_\parallel=\mathbf{0}$ in the QW without impurities. For the even states of an on-center donor impurity this is always the case, whereas it is not for the odd states when the QW is sufficiently narrow ($L<50$ Å for $x=0.3$). In the latter situation, however, most of the contribution originates from the lowest continuum states (obtained with the procedure described above), and an expression for the contribution of the region of the continuum higher than $\Lambda_{\max}$ similar to Eq.

(12) can still be proved.

The impurity states are classified according to the symmetry of the EM Hamiltonian (1); this is the point group $D_{\infty h}$ for on-center impurities and reduces to $C_{\infty v}$ for impurities elsewhere. The irreducible representations of these groups are classified by $\Lambda=|m|$, which is denoted by Σ if $m=0$ and Π if $m=\pm1,\pm2,\ldots$. There are two types of representations Σ, characterized by the parity (+ or −) under a σ_v operation (the reflection with respect to a plane containing the QW axis), for both on- and off-center impurities. The representations Σ^- do not have a corresponding bulk state for hydrogenlike systems, because for such systems the envelope function is always even under σ_v, and therefore there are no such donor states belonging to Σ^- in a QW structure; in the following we use the symbol Σ to denote the representations of the Σ^+ type. In addition, the irreducible representations of the point group $D_{\infty h}$ are classified by the parity with respect to the σ_h operation (the reflection $z\rightarrow -z$), which we indicate by the subscript g or u for even and odd states, respectively. The complete classification of a donor state is then given by $N\Lambda_{\sigma_h}$, where $N=1,2,3,\ldots$ distinguishes the states with the same symmetry.

In the two-dimensional limit (very thin GaAs slab and infinitely high potential barriers) the exact solution of the problem[14] is recovered with our expansion procedure. In the opposite limit we have verified that the bulk donor spectrum in GaAs is achieved with better than 1% accuracy when L is very large with respect to a^*.

A first description of this method with preliminary results was presented at the Third International Conference on Shallow Impurities in Semiconductors (Linköping, Sweden, 1988).[15]

The extension of the method to the acceptor states has been carried out, and it has been found that the states of the QW in the continuum must always be considered, because the effective masses are larger, and because the four components of the envelope function require the use of states of both parities, even for on-center impurities.

III. RESULTS AND DISCUSSION

We have performed calculations for QW's of various well thicknesses L, with the impurity located at different positions inside the well. For the band mismatch we used the value $V_0=0.65\Delta E_g$,[16] where $\Delta E_g=1.247x$ eV.[17] The electron effective mass was taken to be $m_1^*=0.067m_e$ in the well and $m_2^*=(0.067+0.083x)m_e$ in the barriers;[17] the dielectric constants were taken to be $\epsilon_1=12.53$ in the well and $\epsilon_2=12.53-2.73x$ in the barriers.[10] The best choice for the exponents α_j in Eq. (9) was found to be a geometrical progression with ratio 1.6, centered around the value $\alpha=1.5/a^*$; when ten exponents are used the ratio between the extreme values of the α_j is ~ 110.

In Fig. 1 we present the energies (relative to the minimum of the first subband, at $\mathbf{k}_\parallel=\mathbf{0}$) of the lowest Σ_g states, for an on-center impurity in QW's of various thicknesses and of composition $x=0.3$. The lowest Π_g states are presented in Fig. 2. The general behavior

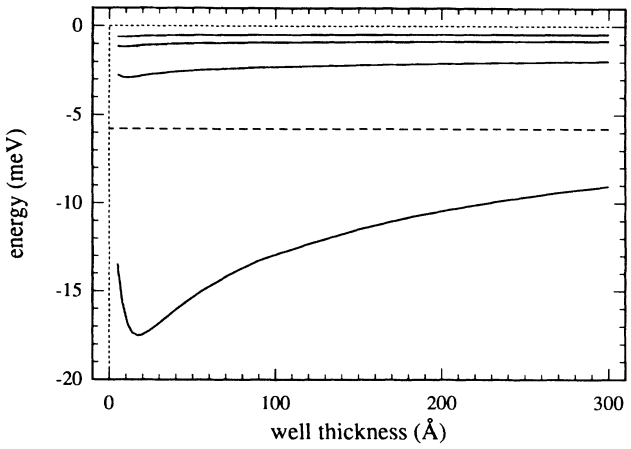

FIG. 1. Energies of the ground and lowest excited states of symmetry Σ_g ($|m|=0$, even parity under a $z\rightarrow -z$ reflection), as a function of the well thickness L, for an on-center impurity and for $x=0.3$. The energies are referred to the bottom of the first subband in the QW.

agrees with that already pointed out by many authors,[1-7] but our numerical values give consistently larger binding energies, as expected from the improved accuracy of the variational procedure. Since we use the eigenstates of the QW at $\mathbf{k}_\parallel=\mathbf{0}$ as basis functions, we cannot apply our method to verify the limit value $L=0$ for finite values of the barrier height V_0. Anyway, our method works for large as well as small values of L, down to one monolayer; as the convergence indicates, we expect for all the energy levels presented in this work a degree of accuracy higher than 1%. As we mentioned before, the two-dimensional energy spectrum is exactly achieved with our trial functions in the case of infinitely high barriers, i.e., for $V_0=\infty$.

To test the effect of taking into account the different effective masses and dielectric constants of the two media, we show in Fig. 3 the ground-state energies (rela-

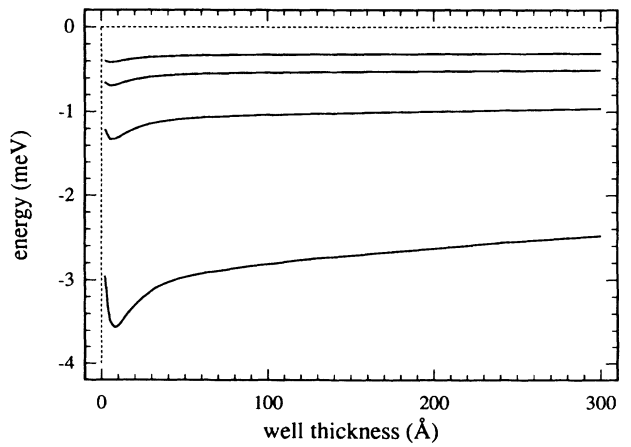

FIG. 2. Energies of the lowest excited states of symmetry Π_g ($|m|=1$, even parity under a $z\rightarrow -z$ reflection), as a function of the well thickness L, for an on-center impurity and for $x=0.3$. The energies are referred to the bottom of the first subband in the QW.

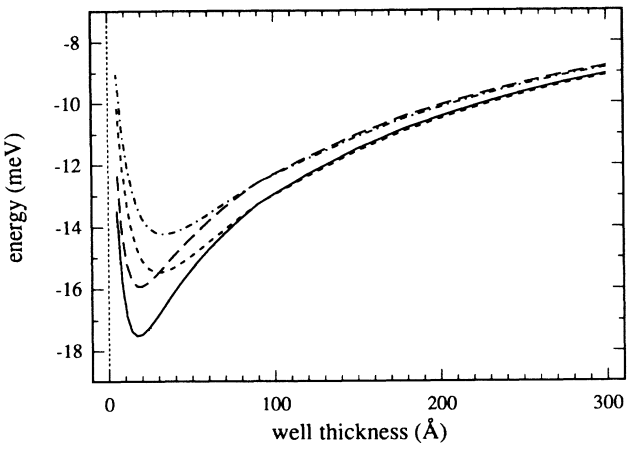

FIG. 3. Energy of the ground state $1\Sigma_g$ (corresponding to the $1s$ bulk state), as a function of the well thickness L, for an on-center impurity and for $x=0.3$ (solid line). With the solid line we show the results obtained by using the proper values of the dielectric constants and effective masses in the well and barriers materials. With dashed lines we show the analogous results when approximations in the parameters ϵ_2, m_2^* are used: long-dashed for $\epsilon_2=\epsilon_1$, short-dashed for $m_2^*=m_1^*$, and dot-dashed for both approximations. The energy is referred to the bottom of the first subband in the QW.

tive to the minimum of the first subband) obtained by using different approximations for the mismatch of the dielectric constant ϵ and of the effective mass m^* at the interfaces between the two materials. We consider four cases corresponding to the use of various sets of parameters: in particular, we show the effect of the choices, often employed in the literature, of $\epsilon_2=\epsilon_1$ and (or) $m_2^*=m_1^*$. The difference between the approximations $\epsilon_2=\epsilon_1$, $m_2^*=m_1^*$, and the full calculation depend on the well thickness L; the use of the appropriate parameters increases the binding energy considerably, and this effect is more relevant the lower the value of L ($\sim 6\%$ at $L\sim 100$ Å, $\sim 20\%$ at the minimum of the curve).

In particular, we remark that the correction introduced by the appropriate use of different values of the dielectric constants decreases slowly for increasing well thickness L, in spite of the fact that the probability p of finding the electron in the barriers becomes negligibly small. This is due to the effect of the image charges: in fact, if we represent the confinement effect by the enhancement factor $A(L)$, such that the binding energy of an on-center donor impurity is $E_0=A(L)$ Ry*, an estimate of the first-order correction gives

$$\frac{\Delta E}{E_0}\sim\left[2p+(1-p)\frac{a^*}{A(L)L}\right]\frac{\Delta\epsilon}{\epsilon_1}\ , \tag{13}$$

where the expression within the large parentheses is dominated by the second term, which describes the interaction of the electron inside the well (with probability $1-p$) with the first image charges in the barriers. We observe that the relative correction is proportional to $\Delta\epsilon/\epsilon_1\simeq 0.22x$, the proportionality factor being about a constant of order unity over a large range of values of the well thickness L. Numerical results supporting this description can be found in Table I, where we compare the correction $\Delta E/E_0$ in QW's of different well thicknesses, for two values of the Al concentration in the barriers: $x=0.3$ and 0.4.

TABLE I. Composition dependence of the ground-state binding energy of an on-center donor impurity in a GaAs-$Ga_{1-x}Al_xAs$ QW. In the first two columns we specify the Al concentration in the barriers and the well thickness. For each case we present the result obtained by using the approximation $\epsilon_2=\epsilon_1$ for the dielectric constant in the barriers (E_0) and that obtained by using the proper value of ϵ_2 (E), the absolute and the relative difference between the two results ($\Delta E=E-E_0$ and $\Delta E/E_0$).

x	L (Å)	E_0 ($\epsilon_2=\epsilon_1$) (meV)	E ($\epsilon_2\neq\epsilon_1$) (meV)	ΔE (meV)	$\Delta E/E_0$
0.3	30	15.54	16.87	1.33	8.6%
0.3	50	14.38	15.41	1.03	7.2%
0.3	75	13.20	13.99	0.79	6.0%
0.3	100	12.26	12.91	0.65	5.3%
0.4	30	16.14	18.01	1.87	11.6%
0.4	50	14.69	16.10	1.41	9.6%
0.4	75	13.39	14.47	1.08	8.1%
0.4	100	12.40	13.28	0.88	7.1%

The case of off-center impurities is exemplified in Table II, where the ground-state binding energy of a donor impurity in a QW of thickness $L=100$ Å and composition $x=0.3$ is presented for four values of the impurity position z_0. The calculation is carried out using appropriate values for the parameters m_2^* and ϵ_2, but the approximation $\epsilon_2=\epsilon_1$ is also shown, and the magnitudes of the absolute and relative corrections are indicated. We note that the absolute value of the correction introduced by β in Eq. (2) is nearly constant, whereas the relative correction increases as the impurity position approaches an interface. We conclude that in the calculation of donor states in GaAs-$Ga_{1-x}Al_xAs$ QW's the usual approximations $\epsilon_2=\epsilon_1$ and $m_2^*=m_1^*$ are not justified if one considers high values of the Al concentration ($x\sim 0.3$) and narrow QW's ($L\lesssim 80$ Å), which are the most relevant cases for spatial confinement.

To our knowledge there is only one paper, by Mailhiot *et al.*,[2] which takes into account the different dielectric constants of GaAs and $Ga_{1-x}Al_xAs$. In that paper seven

TABLE II. Impurity position dependence of the ground-state binding energy of a donor impurity in a GaAs-$Ga_{0.7}Al_{0.3}As$ QW of thickness $L=100$ Å. In the first column we specify the impurity position. For each case we present the result obtained by using the approximation $\epsilon_2=\epsilon_1$ for the dielectric constant in the barriers (E_0) and that obtained by using the proper value of ϵ_2 (E), the absolute and the relative difference between the two results ($\Delta E=E-E_0$ and $\Delta E/E_0$).

z_0 (Å)	E_0 ($\epsilon_2=\epsilon_1$) (meV)	E ($\epsilon_2\neq\epsilon_1$) (meV)	ΔE (meV)	$\Delta E/E_0$
0	12.26	12.91	0.65	5.3%
20	11.19	11.83	0.64	5.7%
40	8.98	9.62	0.64	7.1%
50	7.97	8.60	0.63	7.9%

modified Gaussian functions are used and only the ground state and a few excited states of the s symmetry are considered. Our results for the binding energy of the ground state compare well with those of Ref. 2 only for $L > 200$ Å, whereas our result is larger by about 1.6 meV for $L \sim 60$ Å and the difference is still greater for smaller values of L. This difference is difficult to explain (we note that the same parameters have been used in the comparison); we believe that our variational approach is much more suitable for the symmetry of the problem, particularly in the case of narrow wells.

Our results for the binding energy of the ground state for $\epsilon_2 = \epsilon_1$ are in agreement with those of Ref. 7, when we use the same parameters as in that reference and we put only one subband in the expansion set. We can compare our results for $\epsilon_2 = \epsilon_1$ also with those of Priester *et al.*[4] by considering only the first subband and by searching numerically the minimum in the diagonal of the Hamiltonian matrix: this is equivalent to optimizing the variational parameter λ in the simple trial function $\exp(-\lambda\rho) f_{1,\mathbf{k}_\parallel=0}(z)$. By using the same parameters as theirs we find the same results, the binding energy being smaller than that reported in Fig. 3 due to the oversimplified variational treatment.

We note that often in the literature the neglect of the dielectric-constant mismatch was justified *a posteriori* on the basis of a comparison of the results, obtained by using different methods and different parameters, with those of Ref. 2. In our opinion the present results will serve to clarify this misunderstanding and give a complete assessment of the effect of the dielectric-constant mismatch, which turns out to be much larger than previously assumed.

In Fig. 4 we present the energy (referred to the minimum of the lowest odd subband, at $\mathbf{k}_\parallel = \mathbf{0}$) of the lowest Σ_u state for an on-center impurity in a QW with

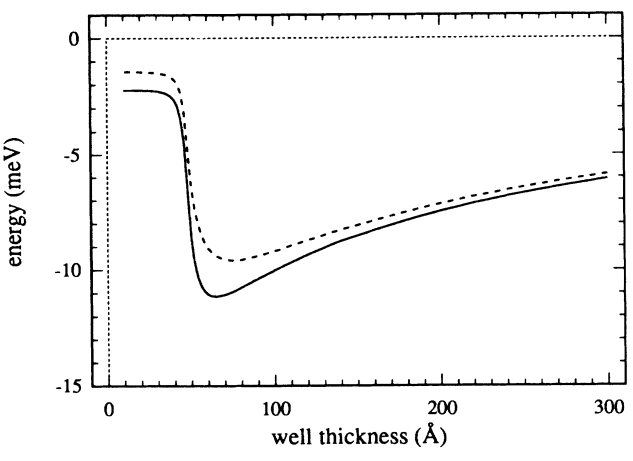

FIG. 4. Energy of the lowest state of symmetry Σ_u (corresponding to the $2p_0$ bulk state), as a function of the well thickness L, for an on-center impurity and for $x = 0.3$ (solid line). The energy is referred to the bottom of the second subband in the QW (odd under $z \to -z$ reflection), or, for narrow wells ($L < 50$ Å), to the onset of the continuum (i.e., to V_0). The dashed line shows the results of the same calculation when the approximations $\epsilon_2 = \epsilon_1$ and $m_2^* = m_1^*$ are used.

$x = 0.3$, for different values of L. The values for $L < 50$ Å are obtained by using in expansion (9) only the states of the continuum, since no bound odd parity states exist without the impurity, and the energy is referred to the onset of the continuum, i.e., to V_0. In the limit $L \ll a^*$ the energy tends to the same value as the $2p_0$ state in bulk $Ga_{0.7}Al_{0.3}As$, whereas in the opposite limit (not considered in Fig. 4) the energy tends to the value of the $2p_0$ state in bulk GaAs. The dashed line shows the results obtained with the approximation $\epsilon_2 = \epsilon_1$ and $m_2^* = m_1^*$.

The binding energy of the lowest odd state was previously calculated for $L > 50$ Å using various approximations for the trial function;[18,19] our approach, however, considers the contribution of all odd subbands, whose interaction depends on the well thickness, and therefore allows a description of the impurity states at all well thicknesses. We note that although this state is resonant with the continuum of the first (even) subband, the decay is forbidden by parity.

IV. INFRARED ABSORPTION

The above results allow for a computation of the far-infrared absorption by donor impurities in a QW. General considerations, with a discussion of the line broadening produced by the distribution of the impurities inside the well, are given by Greene and Lane,[20] who considered the absorption of x polarized radiation. We now consider also the case of z polarized radiation, for which the relevant quantity is the matrix element of z between the envelope functions.

In Fig. 5(a), we present the square of the dipole matrix element between the states 1Σ and 2Σ for radiation polarized in the z direction, for all positions of the impurity inside a QW of thickness $L = 400$ Å. For comparison, the corresponding curve for the transition $1\Sigma \to 1\Pi$ (optically active in the case of x polarized radiation) is shown in Fig. 5(b), using the same units as in Fig. 5(a). In the case of the $1\Sigma \to 2\Sigma$ transition, the matrix element is zero at $z_0 = 0$: for an on-center impurity both states have Σ_g symmetry and parity forces the matrix element to vanish. Away from the center the matrix element remains still small, being about an order of magnitude smaller than that of the transition $1\Sigma \to 1\Pi$ for x polarization, which is parity allowed for all impurity positions. The reason for this great difference is that, although there are as many as nine discrete subbands in this large QW, the main contribution to the envelope functions of both states involved in the transition is given by the first subband, for which the matrix element of z vanishes by parity. In Fig. 5(a) a maximum is reached near the interface, at $z_0 \simeq 130$ Å, in contrast with the curve for x polarization, in Fig. 5(b), which is monotonically increasing. The decrease of the z matrix element and the increase of the x matrix element, when the impurity approaches an interface, is an effect of the confinement of the electron inside the well: when the impurity is near the interface, the distance being of the order of the effective Bohr radius a^*, the envelope function is somewhat compressed along the z direction and the matrix element of z is therefore reduced, whereas the matrix element of x is enhanced. In

the case of x polarization, the dependence of the squared matrix element of x on the impurity position, Fig. 5(b), agrees with that reported by Greene and Lane.[20]

Given an impurity distribution in the well, the absorption coefficient can be computed, for different polarizations, for all transitions between the impurity states. In order to compare with the experiment of Jarosik *et al.*[21] we have computed the absorption coefficient versus photon energy for a GaAs-$Ga_{1-x}Al_xAs$ QW with $L=210$ Å, $x=0.31$, and an impurity distribution (a Gaussian about the center with half-width $=1/6L$) close to the declared one. In Fig. 6 we show the calculated line shape due to the $1\Sigma\rightarrow n\Pi$ transitions with x polarization. A phenomenological width $\Gamma=0.7$ meV has been introduced by replacing the δ function $\delta(E_{fi}-\hbar\omega)$ with a Lorentzian line shape in the computation of the absorption coefficient. We note a main peak centered at 7.5 meV, corresponding to the transition $1\Sigma\rightarrow 1\Pi$. The asymmetry of the peak depends on the different broadening mechanisms at each side: the large impurity distribution in the well gives rise to the long tail on the low-energy side, whereas the structures on the high-energy side are due to transitions from the ground state 1Σ to higher excited states $N\Pi$. The experimental results are not sufficiently accurate to enable us to compare the line shape; however, the observed position of the peak,[21] $E=7.3$ meV, coincides with the calculated one within the given experimental error.

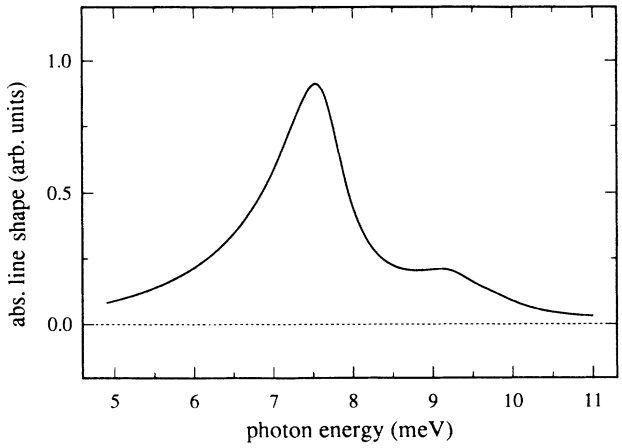

FIG. 6. Computed line shape of the absorption coefficient for x-polarized radiation, in a QW with $L=210$ Å and $x=0.31$. The doping distribution is taken to be a Gaussian about the center of half-width $=\frac{1}{6}L$, in agreement with Ref. 21.

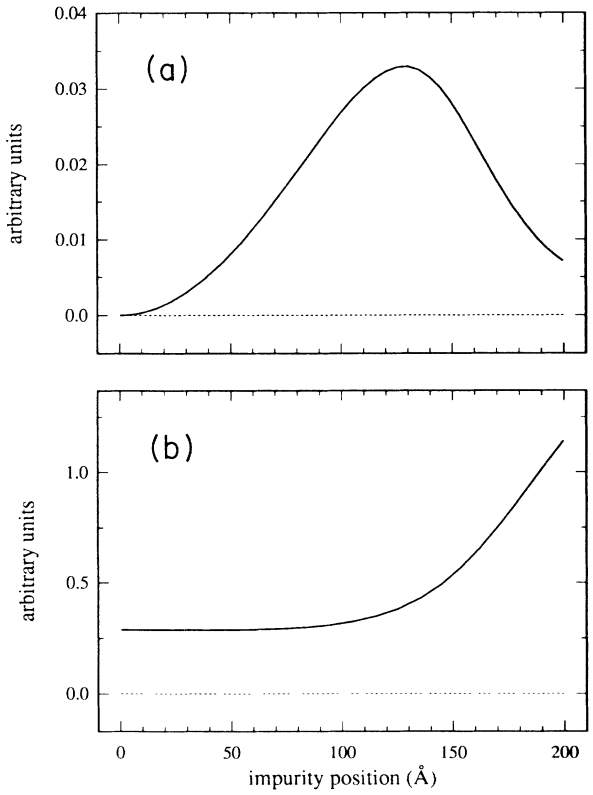

FIG. 5. (a) Computed value of $|\langle 1\Sigma|z|2\Sigma\rangle|^2$, the square of the relevant matrix element for the $1\Sigma\rightarrow 2\Sigma$ transition (with z-polarized radiation), as a function of the impurity position z_0, for $L=400$ Å and for $x=0.3$. (b) Computed value of $|\langle 1\Sigma|x|1\Pi\rangle|^2$ for the $1\Sigma\rightarrow 1\Pi$ transition (with x-polarized radiation), as a function of the impurity position z_0. The QW parameters are the same as in (a).

V. CONCLUSIONS

In this paper we present a variational method to compute the states of a donor impurity in a GaAs-$Ga_{1-x}Al_xAs$ quantum well. The method is based on the expansion of the envelope function in the subband states of the QW without impurities, which insures that the boundary conditions are satisfied. The convergence of the method is verified by introducing in the expansion set also the states of the continuum. Although their contribution to the donor states is in general small, it is found that they are needed in the computation of odd states in narrow QW's.

We consider the corrections due to the different values of the effective masses and of the dielectric constants in the well and in the barriers. The latter correction in particular is found to be quite sizable for high values of the Al concentration ($x\sim 0.3$) and for narrow well thicknesses ($L\lesssim 80$ Å). The correction is found to decrease slowly with increasing values of L, because of the long-range Coulomb interaction between the electronic charge in the well and the image charges in the barriers. We conclude that the usual approximation $\epsilon_2=\epsilon_1$ is not justified even in this case of materials with very similar dielectric constants.

The ground and the lowest excited states of each symmetry are obtained for various values of the QW and impurity parameters (well thickness L, Al concentration x, and impurity position within the well z_0). These results allow for the computation of the far-infrared absorption in n-type GaAs-$Ga_{1-x}Al_xAs$ quantum wells; this is carried out for both polarizations of the incident rediation (parallel and perpendicular to the QW axis). The position of the absorption peak is in good agreement with available experimental data.

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APPENDIX

Our purpose here is to compute the contribution of the states of the continuum which were not explicitly considered in the Hamiltonian matrix in Eq. (10). For this calculation it is better to consider the basis set in the alternative form (7):

$$\psi_{\Lambda\mathbf{k}_\parallel}=\exp(i\mathbf{k}_\parallel\cdot\mathbf{r}_\parallel)f_{\Lambda\mathbf{k}_\parallel}(z)\ , \tag{A1}$$

where the continuous index Λ is used instead of the discrete one n. The functions $\psi_{\Lambda\mathbf{k}_\parallel}$ are eigenfunctions of

$$H_{\rm QW}\equiv\frac{\hbar^2\mathbf{k}^2}{2m^*}+V_{\rm QW}\ , \tag{A2}$$

with eigenvalues $\Lambda+\hbar^2\mathbf{k}_\parallel^2/2m^*$. In order to apply perturbation theory we take as zeroth-order Hamiltonian

$$H_0=P_1HP_1+P_2H_{\rm QW}P_2\ , \tag{A3}$$

where P_1 and P_2 are projection operators onto the subspace of the $\psi_{\Lambda\mathbf{k}_\parallel}$ with $\Lambda<\Lambda_{\max}$ and $\Lambda>\Lambda_{\max}$, respectively. The eigenfunctions of H_0 include approximate donor states, as obtained by solving the eigenvalue problem in Eq. (10), and the eigenstates of the QW without impurities $\psi_{\Lambda\mathbf{k}_\parallel}$ with $\Lambda>\Lambda_{\max}$. The perturbation Hamiltonian is

$$H_1\equiv H-H_0=P_1HP_2+P_2HP_1+P_2V_{\rm imp}P_2\ . \tag{A4}$$

Let us consider the ground state of an on-center donor in a QW and the zeroth-order approximation of the envelope function F_0, with energy E_0. By application of standard second-order perturbation theory to include the correction to the energy due to the states of energy higher than $\Lambda_{\max}$, we obtain

$$E=E_0+\int_{\Lambda_{\max}}^{\infty}d\Lambda\, g(\Lambda)\sum_{\mathbf{k}_\parallel}\frac{|\langle\Lambda,\mathbf{k}_\parallel|H_1|F_0\rangle|^2}{E_0-(\Lambda+\hbar^2\mathbf{k}_\parallel^2/2m^*)}\ , \tag{A5}$$

where $g(\Lambda)\propto\Lambda^{-1/2}$ is the one-dimensional density of states. In order to compute the matrix elements of H_1, we make the following approximations:

$$F_0(\mathbf{r})=\begin{cases}C\ \cos(k_0z)\exp(-\alpha\rho) & \text{for } |z|<L/2\ ,\\ 0 & \text{for } |z|>L/2\ .\end{cases} \tag{A6}$$

$$f_{\Lambda\mathbf{k}_\parallel}(z)=D\exp\left[i\frac{(2m^*\Lambda)^{1/2}}{\hbar}z\right]\quad \text{for}\Lambda\gg V_0\ , \tag{A7}$$

where $k_0\sim\pi/L$, $\alpha\sim1/a^*$, and C,D are normalization constants; in the calculation we suppose that

$$\Lambda_{\max}\gg\frac{\hbar^2\alpha^2}{2m^*}\ ,\frac{\hbar^2k_0^2}{2m^*},V_0\ . \tag{A8}$$

By performing the integral in Eq. (A5) we obtain the result reported in the text as Eq. (12).

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