Binding energies of ground and excited states of shallow acceptors in $GaAs/Ga_{1-x}Al_xAs$ quantum wells

Samuele Fraizzoli
Institut Romand de Recherche Numérique en Physique des Matériaux (IRRMA), PHB-Ecublens, CH-1015 Lausanne, Switzerland and Scuola Normale Superiore, I-56100 Pisa, Italy

Alfredo Pasquarello
Institut de Physique Théorique, Ecole Polytechnique Fédérale de Lausanne, PHB-Ecublens, CH-1015 Lausanne, Switzerland

(Received 10 May 1990)

We calculate binding energies of shallow acceptors in $GaAs/Ga_{1-x}Al_xAs$ quantum wells (QW's) for varying well widths. Variational calculations are performed in the framework of a multiband effective-mass theory, which accounts for the mixing between heavy and light holes. The Hamiltonian also takes into account the mismatch between the band parameters and the dielectric constants of well and barrier materials. The envelope function is expanded into a basis set consisting of products of two-dimensional hydrogeniclike functions and impurity-free QW eigenfunctions at $\mathbf{k}_{||} = \mathbf{0}$. QW eigenfunctions of the continuum are included till convergence of the acceptor energies is reached. The present method is suited for ground as well as excited acceptor states of Γ_6 and Γ_7 symmetry. We do not include central-cell effects, but give the dependence of the on-center density as a function of the well width in order to estimate these corrections. Comparison with recent experiments, which determine the $1s - 2s$ energy separation, shows very good agreement.

Impurity states in quantum wells (QW's) have extensively been studied with a variety of different techniques: photoluminescence, [1,2,3] magnetospectroscopy,[4] far-infrared absorption,[5] and resonant Raman scattering.[6,2,3] Recently Holtz *et al.*[2,3] have performed measurements on acceptor states with two different techniques, two-hole transitions and Raman scattering, which have provided a very accurate determination of the energy separation between $1s$ and $2s$ acceptor states.

Early calculations of impurity states in quantum wells were based on a one-band effective-mass approximation.[7,8,9] This one-band approximation is particularly suited for donor states and fails in the more complicated case of acceptor impurities, as discussed in detail by Greene and Bajaj.[10] The acceptor states are associated to the valence band, which in the bulk is fourfold degenerate at the Γ point and has a nonspherical dispersion. Contrary to the case of donor states which are mainly associated to one QW subband, in the case of acceptors, because of their higher binding energy, the full QW dispersion should be accounted for. Moreover, in the case of acceptors, the effect of central-cell corrections has to be considered.

The first calculations coping with the complicated valence-band structure were performed by Masselink *et al.*,[11] who used a four-band effective-mass Hamiltonian.[12] These calculations turned out to be more appropriate for the ground state than for the excited states.[13,14] Subsequently, Pasquarello *et al.*[13] used a **k**-space formalism in order to calculate excited acceptor states. However, s-type acceptor states were given only approximatively and it was shown that QW continuum states had to be considered in order to obtain more precise results. The validity of the results of Masselink *et al.*[11] was questioned for narrow well widths.[13] Very recently calculations on acceptor states have been performed by Einevoll and Chang using an effective tight-binding method.[14] This formulation is essentially a discretized version of the effective-mass theory and contains a free parameter which is fitted on experimental bulk results for the ground-state energy. The advantage of this formulation is that it is suited for the case of very narrow QW's in which the effective-mass approximation is expected to break down. The validity of the effective mass approximation in the limit of narrow wells has been examined in Refs. 15 and 16. Einevoll and Chang claimed that usual effective-mass formulations are too complicated to take properly into account the valence-band degeneracy as well as the position dependence of the material parameters.

In this paper, we present calculations in the effective-mass approximation for s-type ground and excited acceptor states in $GaAs/Ga_{1-x}Al_xAs$ QW's with well widths ranging from 50 Å to 200 Å. The effective-mass approximation is expected to be valid in this range of well widths.[15,16] We have used a four-band effective-mass formulation in order to cope with the degenerate valence-band structure. Because of the choice of a simple basis set consisting of products of two-dimensional hydrogeniclike functions and impurity-free QW eigenfunctions at $\mathbf{k}_{||} = \mathbf{0}$, it has been possible to include the effect due to the mismatch of band parameters and dielectric constants. In order to have converging binding energies for

the acceptor states, it has been necessary to include QW continuum functions. Despite the large set of basis functions, this formulation is very efficient because of the important advantage that most of the integrals which appear in the matrix elements can be carried out analytically. The same procedure has been applied successfully in the more simple case of donor impurities.[17]

The acceptor states in a quantum well grown along the [001] direction (z axis) are described by the 4×4 matrix operator:

$$H = H^{\text{kin}} + H^{\text{QW}} + H^{i}, \tag{1}$$

where H^{kin} represents the kinetic energy and is given by the Luttinger-Kohn Hamiltonian,[12] H^{QW} is a square-well potential which represents the confinement due to the band discontinuity, and H^{i} stands for the Coulomb potential of the on-center acceptor charge as well as of the infinite set of image charges, originated by the dielectric mismatch. The Luttinger parameters[18] in H^{kin} correspond to those of the well material for $|z| < L/2$ and to those of the barrier material in the other regions. In the Hamiltonian (1) we have neglected self-energy terms deriving from the dielectric mismatch.[19] The neglected terms shift the energy levels of the hole in both the acceptor and the valence-subband state, and therefore binding energies are not essentially affected. We have checked the effect of the neglected terms in first-order perturbation theory and found that in the considered well-width range the acceptor binding energies are changed by less than 0.1 meV.

The symmetry of an on-center acceptor in a QW is D_{2d}. All the acceptor states are two-times degenerate and transform like Γ_6 or Γ_7.[20] However, the effective-mass Hamiltonian has a higher symmetry. The Luttinger Hamiltonian is taken in the axial approximation which has been shown to be accurate in the case of calculations of acceptor binding energies.[13] The acceptor states can therefore be classified according to the z component of angular momentum m. Degenerate states have opposite angular momentum. Parity with respect to inversion is another good quantum number. The acceptor states can therefore be classified by $(|m|, \pm)$. Reflection in the $z = 0$ plane is also a symmetry of the acceptor system, but is related to the previous ones. A detailed symmetry analysis can be found in Ref. 13. Acceptor states of s-type symmetry are given by $(\frac{3}{2},+)$ for Γ_6 (symmetry of heavy-hole ground states) and by $(\frac{1}{2},+)$ for Γ_7 (symmetry of light-hole ground states).

The four-component envelope function $F^{m,s}$, where s is the spin index which runs from $-\frac{3}{2}$ to $\frac{3}{2}$, is developed in the complete set of basis functions which are separable in ρ and z:

$$F^{m,s}(\rho, z) = e^{i(m-s)\theta} \sum_{n} R_n^{m,s}(\rho) g_n^s(z), \tag{2}$$

where g_n^s are impurity-free QW eigenfunctions at $\mathbf{k}_{||} = \mathbf{0}$ including discrete as well as continuum QW states. The latter states are accounted for by discretizing the continuum introducing sufficiently distant infinite barriers. The functions g_n^s satisfy current conserving boundary conditions at the interfaces. We note that the four-component g_n^s have only one nonvanishing component, which has a different spin-index according to the QW subband it represents. In our calculations we have chosen the g_n^s to have a definite parity with respect to the 4×4 matrix operator which represents the reflection in the plane $z = 0$.[21] The radial functions $R_n^{m,s}$ are developed in an expansion of symmetry-adapted decreasing exponentials:

$$R_n^{m,s}(\rho) = \rho^{|m-s|} \sum_{l} A_{nl}^{m,s} e^{-\alpha_l \rho}, \tag{3}$$

where the exponents α_l are chosen to cover the relevant physical region, and where the $A_{nl}^{m,s}$ are variational parameters.

Using the standard variational method, the eigenvalue problem can be turned into a set of coupled algebraic equations for the $A_{nl}^{m,s}$. The calculation of the matrix elements of the kinetic energy is straightforward and can be carried out analytically. The matrix elements of the Coulomb potential are more complicated. The calculation of the latter matrix elements can be simplified using the following integral expression for the Coulomb potentials of H^{i} which decouples z and ρ coordinates:

$$\frac{1}{(\rho^2 + z^2)^{1/2}} = \int_0^\infty ds\, e^{-|z|s} J_0(\rho s), \tag{4}$$

where J_0 is a Bessel function of order zero. In this way all integrals over the coordinates can be carried out analytically.[17] The infinite series of image charges give a geometric series which can be summed analytically as well. Only the final integral of Eq. (4) is evaluated numerically.

In the numerical calculations, we have used the Luttinger parameters $\gamma_1 = 6.85$, $\gamma_2 = 2.1$, $\gamma_3 = 2.9$ and the dielectric constant $\epsilon = 12.53$ for GaAs, and $\gamma_1 = 3.45$, $\gamma_2 = 0.68$, $\gamma_3 = 1.29$, $\epsilon = 9.8$ for AlAs.[22] The parameters for $Ga_{1-x}Al_xAs$ are obtained by linear interpolation. The band discontinuity is taken to be $\Delta E_v = 0.35 \times 1247 \times x$ meV,[23] where an offset ratio between conduction and valence band of 65:35 has been assumed.

In Fig. 1 we present acceptor energies of on-center acceptors in $GaAs/Ga_{0.7}Al_{0.3}As$ QW's for well widths ranging from 50 Å to 200 Å. We have reported the acceptor energies of ground and first excited s-type acceptor states of Γ_6 and Γ_7 symmetry. The acceptor energies are given with respect to the top of the first heavy-hole subband. The energies of the Γ_6 and Γ_7 ground states increase for decreasing well width. In contrast with previous effective-mass calculations,[11] the energy of the first excited Γ_6 state is almost constant and even increases slightly for decreasing well widths. It is well known that in a simple hydrogenic model, whereas the energy of the ground state is enhanced by a factor of 4 going from the three- to the two-dimensional limit, the energy of the first excited state is only increased by a factor of $\frac{16}{9}$. In the realistic case of finite barriers this increase is reduced, analogously, as found for donor impurities.[17] On the other hand the acceptor energy of the first excited

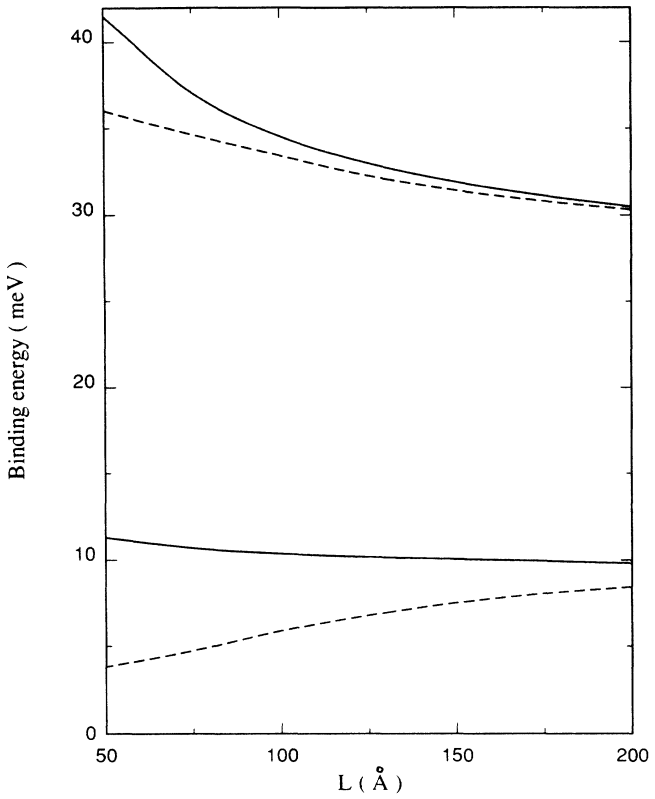

FIG. 1. Energy levels with respect to the first heavy-hole subband of on-center acceptors in $GaAs/Ga_{0.7}Al_{0.3}As$ quantum wells as a function of the well width. We report s-type ground states and first excited states of Γ_6 (solid) and Γ_7 (dashed) symmetry.

Γ_7 state decreases for decreasing well width. This is understood because this state is mainly associated to the light-hole subbands. In fact, if the acceptor energies are given with respect to the first light-hole subband, the energy of the first excited Γ_7 state is found to increase for decreasing well width. We note that not only the ground states but also the first excited states have higher binding energies with respect to the results obtained in the k-space formulation.[13] The results in Fig. 1 are in good agreement with recent calculations, obtained with an effective tight-binding method.[14]

A comparison of the absolute ground-state energy (with respect to the top of the bulk valence band) obtained at 200 Å with the theoretical bulk value in the same axial approximation[13] shows that our results underestimate the exact binding energy of the ground states by less than 0.2 meV.[24] Better convergence is expected for the excited states as their binding energy is lower. The error due to the axial approximation is estimated to be about 0.5 meV. We therefore believe the overall error of our calculations to be less than 1 meV.

In Fig. 2 we compare, for varying well widths, the calculated transition energies between ground and first excited s-type Γ_6 acceptor states with recent experimental results.[2,3] The experimental data are obtained with two different techniques, two-hole transitions and Raman scattering, and represent the actual more accurate experimental results for the $1s$-$2s$ energy separation. The experimental values correspond to quantum wells which have been centrally doped with Be. Although the calculations have been performed for an ideal acceptor, i.e., without considering central-cell corrections, the theoretical results are in very good agreement with experiment.

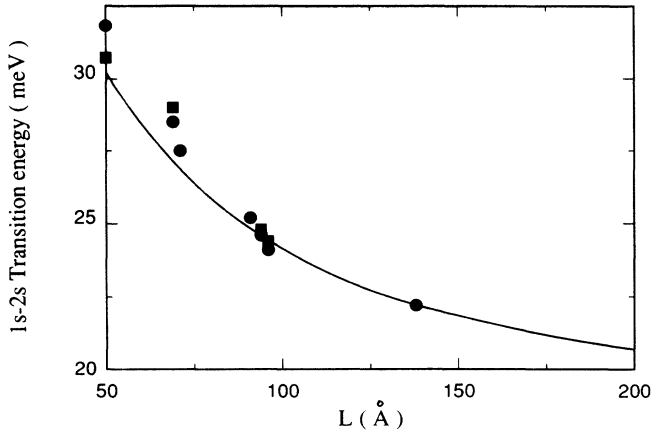

FIG. 2. Comparison between the present theoretical predictions of the energy separation between $1s$ and $2s$ acceptor states of Γ_6 symmetry and results from two-hole transition (discs) and resonant Raman scattering (squares) experiments.[2,3] The transition energy is given as a function of the well width in the case of $GaAs/Ga_{0.7}Al_{0.3}As$ quantum wells.

We discuss now the effect of central-cell corrections in QW's. From our model we deduce a bulk binding energy of 28.3 meV,[24] whereas the experimental bulk value for the Be acceptor is 28.0±0.3 meV.[22] Besides the aforementioned errors in our solution of the effective-mass Hamiltonian (1), there are other effects which are not accounted for by Hamiltonian (1). They are due to coupling to the split-off band, to the spatial dependent screening, and to the chemical shift of the considered impurity.[25] The above comparison shows that there is an almost complete cancellation of all these effects. We expect that this cancellation is effective also in the QW, as long as the acceptor wave function on the impurity site is similar to the wave function in the bulk limit. This is the case for QW's larger than about 100 Å, as can be deduced from the absolute energy of the impurity which remains almost constant in this well width range. A more precise indication of the variation of the acceptor wave function in QW's is given by the charge density on the acceptor site. In Fig. 3, we give this density for s-type ground and first excited states of Γ_6 symmetry. The densities have been normalized with respect to the density of the ground state at 200 Å which is the largest considered well width. The radius of the acceptor ground state being about 20 Å, the density is expected to be constant for large well widths. In fact Fig. 3 shows that for decreasing well widths the density of the ground state on the acceptor site remains almost constant till a well width of about 100 Å (the small oscillations are within our numerical accuracy). For smaller well widths the density increases

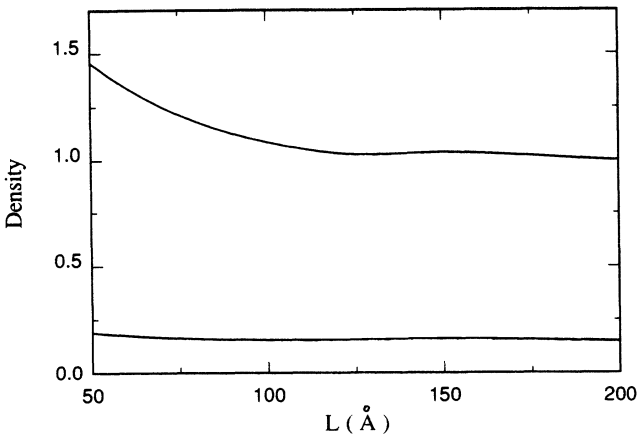

FIG. 3. Charge density on the acceptor site for s-type ground and first excited states of Γ_6 symmetry as a function of the well width in the case of $GaAs/Ga_{0.7}Al_{0.3}As$ quantum wells. The densities have been normalized with respect to the density of the ground state at 200 Å.

reaching at a well width of 50 Å, a value of about 150% the bulk value. The density of the first excited Γ_6 state is found to be almost constant in the considered well-width range. This result compares well with the almost constant binding energy presented in Fig. 1. We therefore expect that in the considered well width, from 50 to 200 Å the central-cell corrections to the $1s$-$2s$ energy separation can be considered constant to a first approximation. Larger discrepancies with respect to the present calculations could arise for well widths less than 100 Å.

In conclusion, we have presented an effective-mass formulation of acceptor states in QW's which is suited for ground as well as excited acceptor states. We have presented binding energies of s-type acceptor states of Γ_6 and Γ_7 symmetry for well widths ranging from 50 Å to 200 Å. The calculated energy separation between $1s$ and $2s$ acceptor states is in very good agreement with transition energies accurately determined by two-hole transitions and Raman scattering in recent experiments on Be-doped QW's.[2,3] The present theory reproduces correctly ground as well as excited states and shows the effectiveness of the usual effective-mass formulation for acceptors in QW's, in contrast to what is reported.[14] The effect of central-cell corrections, which are not accounted for in the model, have been estimated studying the charge density on the acceptor site. We find that for well widths larger than about 100 Å, the overall central-cell correction can be taken equal to its bulk value. We wish to emphasize that a distinct virtue of the present theory lies in the use of a set of basis functions which are separable in the $\mathbf{r}$ coordinates. This fact allows the theory to be extended easily in order to cope with external perturbations such as electric or magnetic fields and uniaxial strain.

We acknowledge interesting and fruitful discussions with L. C. Andreani, A. Baldereschi, F. Bassani, N. Binggeli, and R. Buczko. Support by the European Economic Community under Contract No. ST2J-0254-1-I is gratefully acknowledged. One of the authors (S. F.) acknowledges partial support from the Swiss National Science Foundation under Grant No. 20-5446.87.

[1] R. C. Miller, A. C. Gossard, W. T. Tsang, and O. Munteanu, Phys. Rev. B **25**, 3871 (1982).
[2] P. O. Holtz, M. Sundaram, R. Simes, J. L. Merz, A. C. Gossard, and J. H. English, Phys. Rev. B **39**, 13 293 (1989).
[3] P. O. Holtz, M. Sundaram, K. Doughty, J. L. Merz, and A. C. Gossard, Phys. Rev. B **40**, 12 338 (1989); G. C. Rune, P. O. Holtz, M. Sundaram, J. L. Merz, A. C. Gossard, and B. Monemar (unpublished).
[4] X. Liu, A. Petrou, A. L. Moretti, F. A. Chambers, and G. P. Devane, Superlatt. Microstruct. **4**, 141 (1988).
[5] A. A. Reeder, B. D. McCombe, F. A. Chambers, and G. P. Devane, Phys. Rev. B **38**, 4318 (1988).
[6] D. Gammon, R. Merlin, W. T. Masselink, and H. Morkoç, Phys. Rev. B **33**, 2919 (1986).
[7] G. Bastard, Phys. Rev. B **24**, 4714 (1981).
[8] C. Mailhot, Yia-Chung Chang, and T. C. McGill, Phys. Rev. B **26**, 4449 (1982).
[9] R. L. Greene and K. K. Bajaj, Solid State Commun. **45**, 825 (1983).
[10] R. L. Greene and K. K. Bajaj, Solid State Commun. **53**, 1103 (1985).
[11] W. T. Masselink, Y.-C. Chang, and H. Morkoç, Phys. Rev. B **28**, 7373 (1983); B **32**,5190 (1985).
[12] J. M. Luttinger and W. Kohn, Phys. Rev. **97**, 869 (1955).
[13] A. Pasquarello, L. C. Andreani, and R. Buczko, Phys. Rev. B **40**, 5602 (1989).
[14] G. T. Einevoll and Y.-C. Chang, Phys. Rev. B **41**, 1447 (1990).
[15] C. Priester, G. Allan, and M. Lannoo, Phys. Rev. B **28**, 7194 (1983).
[16] K. J. Moore, G. Duggan, P. Dawson, and C. T. Foxon, Phys. Rev. B **38**, 5535 (1988).
[17] S. Fraizzoli, F. Bassani, and R. Buczko, Phys. Rev. B **41**, 5096 (1990).
[18] J. M. Luttinger, Phys. Rev. **102**, 1030 (1956).
[19] M. Kumagai and T. Takagahara, Phys. Rev. B **40**, 12 359 (1989).
[20] G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, *Properties of the Thirty-Two Point Groups* (MIT Press, Cambridge, MA, 1969).
[21] L. C. Andreani, A. Pasquarello, and F. Bassani, Phys. Rev. B **36**, 5887 (1987).
[22] *Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology*, edited by O. Madelung (Springer, Berlin, 1982), Group III, Vol. 17.
[23] H. C. Casey and M. B. Panish, *Heterostructure Lasers* (Academic, New York, 1978).
[24] The shift of the absolute energy of the ground state with respect to the bulk case, due to the effect of the barriers in a 200-Å QW, has been estimated to be about 0.1 meV by perturbation theory (see Ref. 13). We note that this effect reduces the binding energy.
[25] N. Binggeli, Ph.D. thesis, Ecole Polytechnique Fédérale de Lausanne, Lausanne, 1990.