PHYSICAL REVIEW B VOLUME 26, NUMBER 4 15 AUGUST 1982

Exciton binding energy in quantum wells

G. Bastard,* E. E. Mendez, L. L. Chang, and L. Esaki
IBM Thomas J. Watson Research Center, P. O. Box 218, Yorktown Heights, New York 10598
(Received 15 March 1982)

Variational calculations are presented of the ground exciton state in quantum wells. For the GaAs-GaAlAs system, the results obtained from a trial wave function not separable in spatial coordinates are shown to be valid throughout the entire well-thickness range, corresponding in the thin and thick limits to two- and three-dimensional situations, respectively. For the InAs-GaSb system, in which electrons and holes are present in spatially separated regions, the exciton binding is substantially reduced. In the limit of thin wells, the binding energy is only about one-fourth of the two-dimensional value.

I. INTRODUCTION

The technique of molecular-beam epitaxy has made it possible to grow high-quality heterojunctions and superlattices with prescribed configurations.[1] By cladding GaAs layers with GaAlAs barriers one confines electrons and holes within GaAs wells, resulting in an effective increase of the infrared bandgap up to the visible range.[2,3] The line shape of absorption and luminescence bands of multiple GaAs quantum wells is excitonic.[2,4–7] For a GaAs layer thickness of the order of 30 Å, the exciton motion should be close to the two-dimensional limit, resulting in a binding energy which approaches 4 times the three-dimensional effective Rydberg.

In the InAs-GaSb system[8] the unique band-edge relationship between the two host materials leads to another type of confinement: Although the InAs conduction states overlap the GaSb valence states, the symmetry mismatch between band-edge Bloch functions very effectively confines electrons in InAs and holes in GaSb. This system displays a semiconductor-semimetal transition with an increase of the InAs layer thickness. The observed infrared luminescence in the semiconducting region, for example with a 30-Å InAs layer, is clearly associated with free-electron–heavy-hole recombination.[9] This suggests that the exciton binding energy is very small in these materials and in fact much smaller than the two-dimensional limiting value (~ 5 meV), although the layer thickness involved is only one-tenth of the three-dimensional exciton Bohr radius.

The purpose of this paper is to present *model* calculations of the well thickness dependence of the quantum wells. In Sec. II, we discuss the case of GaAs quantum wells. Miller *et al.*[5] have already considered this problem for a limited range of well thicknesses. They have calculated the $1s$ and $2s$ exciton levels variationally and found a good agreement between the theoretical energy difference $E_{1s}-E_{2s}$ and their experimental data for well thicknesses 30 Å $\leq L \leq$ 150 Å. Here we compare the results obtained from trial wave functions which may or may not be separated into parts associated with directions parallel and perpendicular to the layer plane. The nonseparable function, unlike the separable one which gives valid results only in the thin-layer limit, is applicable to any well width. In Sec. III we consider for simplicity the exciton binding energy for an InAs well confined between two semi-infinite GaSb layers, which represents approximately a segment of the superlattice structure. The spatial separation of electrons and holes gives rise to a significant reduction in the binding energy, which to our knowledge has never been investigated. The calculations by Lozovik and Nishanov[10] of electrons and holes moving in separate planes have some relevance, but lead to a limiting configuration different from the present one of our interest.

II. GROUND BOUND EXCITON STATES IN A GaAs-GaAlAs QUANTUM WELL

In this system electrons and holes are confined in GaAs (Fig. 1), whose layer thickness is denoted by L. We assume the wells to be sufficiently isolated by thick barriers so as to be independent. Then, for nondegenerate and isotropic bands, the exciton Hamiltonian reads

$$\mathcal{H}=\frac{p_{z_e}^2}{2m_e}+\frac{p_{z_h}^2}{2m_h}+\frac{P_X^2+P_Y^2}{2(m_e+m_h)}+\frac{p_x^2+p_y^2}{2\mu}-\frac{e^2}{\kappa[x^2+y^2+(z_e-z_h)^2]^{1/2}}+V_{\text{conf}}(z_e)+V_{\text{conf}}(z_h) \tag{1a}$$

with

$$(m_e+m_h)\vec{R}=m_e\vec{r}_e+m_h\vec{r}_h,\quad \vec{r}=\vec{r}_e-\vec{r}_h\ , \tag{1b}$$

where $m_e,\vec{r}_e$, $m_h,\vec{r}_h$ are the effective masses and positions of electrons and holes, respectively, κ the relative dielectric constant, $\vec{P}$ the center-of-mass momentum, and μ the reduced electron-hole mass in the transverse direction. We have neglected image force effects, which should be rather small because of the nearly equal dielectric constants of GaAs and GaAlAs. The Hamiltonian does not depend on X,Y, and P_X and P_Y are good quantum numbers. They account for the two-dimensional character of the exciton motion in the layer plane.

We will calculate the lowest bound state of the exciton Hamiltonian by a variational procedure. To facilitate the calculations we will assume a perfect confinement of electrons and holes in the well. In the case of shallow donor levels this approximation works well (down to $L\sim 40$ Å) if the Al concentration in $Ga_{1-x}Al_xAs$ is $x\simeq 0.4$.[11] Hence, for this Al composition, we expect it to be a sensible description of the z motion of free electrons as well as that of the heavy holes whose heavier mass offsets the effect of a smaller barrier. Therefore, the electron—heavy-hole exciton binding will be accurately determined within the perfect confinement approximation for almost all the thicknesses

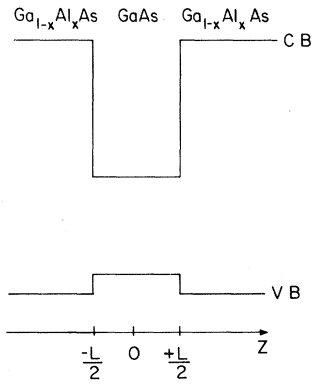

FIG. 1. Quantum-well potential profile along the z axis normal to the interfaces of a GaAlAs-GaAs-GaAlAs heterostructure. The symbols CB and VB denote the conduction- and valence-band edges, respectively.

L which are feasible in practice. The approximation is not as good for electron—light-hole exciton.

We will compare the results obtained from two different trial wave functions; one is separable in z and x,y (ψ_1) and the other is not (ψ_2). Dropping the plane-wave terms associated with P_X and P_Y we take

$$\psi_1=N_1\cos\frac{\pi z_e}{L}\cos\frac{\pi z_h}{L}\exp\left[\frac{-\rho}{\lambda_1}\right], \tag{2}$$

$$\psi_2=N_2\cos\frac{\pi z_e}{L}\cos\frac{\pi z_h}{L}\times\exp\left[-\frac{1}{\lambda_2}[\rho^2+(z_e-z_h)^2]^{1/2}\right], \tag{3}$$

where N_1,N_2 are normalization constants, λ_1,λ_2 trial parameters, and $\rho^2=x^2+y^2$. The separable trial wave function is well suited for narrow well structures as the z localization is provided by the free-particle carrier functions. The nonseparable wave function displays the same feature at low L and is expected to remain valid even in the range of large L where the $|z_e-z_h|$ dependence becomes dominant.

In addition to the binding energy, the expectation values of $|z_e-z_h|$ and ρ^2 are relevant quantities which are helpful to ascertain the accuracy of a trial wave function, as they provide some insight into its spatial extension. These expectation values are readily obtained for ψ_1, namely:

$$\langle\,|z_e-z_h|\,\rangle_1=\langle\psi_1||z_e-z_h||\psi_1\rangle=L\left[\frac{1}{3}-\frac{5}{4\pi^2}\right], \tag{4}$$

$$(\langle\rho^2\rangle_1)^{1/2}=(\langle\psi_1\,|\,\rho^2\,|\,\psi_1\rangle)^{1/2}=\lambda_1\sqrt{3/2}\ . \tag{5}$$

On the other hand, corresponding expressions for ψ_2 are too complicated to be shown here. In Fig. 2 we compare the thickness dependence of the dimensionless binding energy

$$\frac{R_i^*}{R_\infty}=\left[\frac{\hbar^2\pi^2}{2L^2}\left[\frac{1}{m_e}+\frac{1}{m_h}\right]-\min_{\lambda_i}\langle\psi_i\,|\,\mathcal{H}\,|\,\psi_i\rangle\right]\Big/R_\infty,\quad i=1,2 \tag{6}$$

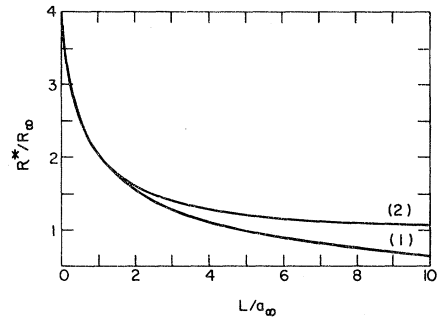

FIG. 2. Dimensionless exciton binding energy R^*/R_∞ is plotted vs the dimensionless well thickness L/a_∞ for GaAlAs-GaAs-GaAlAs heterostructure. The curves labeled (1) and (2) have been obtained using the trial wave functions ψ_1 and ψ_2, respectively.

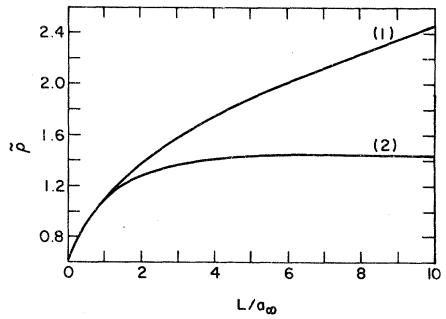

FIG. 3. Dimensionless transverse extension $\tilde{\rho}$ of the exciton wave function is plotted vs the dimensionless well thickness L/a_∞ for a GaAlAs-GaAs-GaAlAs heterostructure. The curves labeled (1) and (2) have been obtained using the trial wave functions ψ_1 and ψ_2, respectively.

where the scaling quantity R_∞ is the three-dimensional effective Rydberg calculated with the transverse mass μ: $R_\infty=\mu e^4/2\kappa^2\hbar^2$. Note that there exist two different values of R_∞, corresponding to electron—light- and electron—heavy-hole excitons. For both ψ_1 and ψ_2 the binding energy R^* goes to $4R_\infty$, when L goes to zero; and the trial parameter λ_1,λ_2 approach $\frac{1}{2}a_\infty$, where a_∞ is the three-dimensional Bohr radius calculated with the transverse mass μ. These are exact results corresponding to the two-dimensional hydrogenic ground state. It is noted that the two-dimensional behavior disappears very quickly: for $L/a_\infty=1$, $R^*\approx 2R_\infty$. Both trial wave functions ψ_1 and ψ_2 give almost identical binding energies for $L\lesssim 1.4a_\infty$. Above this value of L, ψ_2 gives better results than ψ_1 and they become exact in the large L limit, with $R^*(\infty)=R_\infty$. This is not the case for ψ_1, which leads to a binding energy already smaller than R_∞ at $L\gtrsim 4.5a_\infty$ and finally vanishing at infinite L. Furthermore, λ_1 diverges at large L whereas λ_2 remains finite approaching a_∞ at large L. The results obtained with ψ_2 agree essentially with those calculated by Miller *et al.*[5] in the range of L investigated by these authors: $L\lesssim 2.5a_\infty$. However, because of the $|z_e-z_h|$ dependence exhibited by their wave functions their calculations do not provide the correct value in the thick well limit. Therefore, the wave function used by Miller *et al.*[5] displays an intermediate behavior between ψ_1 and ψ_2.

In Figs. 3 and 4, we compare the thickness dependences of the dimensionless quantities $(\langle\rho^2\rangle_i)^{1/2}$ and $\langle|z_e-z_h|\rangle_i$:

$$\tilde{\rho}_i=\frac{1}{a_\infty}(\langle\psi_i|\rho^2|\psi_i\rangle)^{1/2}\ ,\quad i=1,2 \tag{7}$$

$$\tilde{z}_i=\frac{1}{a_\infty}\langle\psi_i||z_e-z_h||\psi_i\rangle\ ,\quad i=1,2\ . \tag{8}$$

Both $\tilde{\rho}_i(L)$ curves (Fig. 3) extrapolate to the exact value $a_\infty\sqrt{3/8}$ at vanishing L. On the other hand, $\tilde{\rho}_1$ diverges at large L, being proportional to λ_1 whereas $\tilde{\rho}_2$ converges to the exact value $a_\infty\sqrt{2}$ in the same limit. Similar features are observed for the $\tilde{z}(L)$ behavior (Fig. 4). This quantity increases linearly with L with the ψ_1 wave function, but with ψ_2 it departs from this straight line for $L\gtrsim\frac{1}{2}a_\infty$ and smoothly increases to the exact value $\frac{3}{4}a_\infty$ at large L. From Figs. 2—4 it can be concluded that the separable wave function ψ_1 is correct only for thin well thickness whereas the nonseparable wave function ψ_2 provides a suitable interpolation between the limits of thin and thick wells. As expected, the difference between ψ_1 and ψ_2 is found more pronounced in the spatial extent

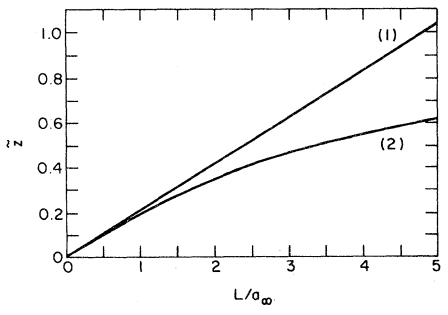

FIG. 4. Dimensionless longitudinal extension $\tilde{z}$ of the exciton wave function is plotted vs the dimensionless well thickness L/a_∞ for a GaAlAs-GaAs-GaAlAs heterostructure. The curves labeled (1) and (2) have been obtained using the trial wave functions ψ_1 and ψ_2, respectively.

of the wave functions than in the energies.

The near-band-gap absorption and luminescence spectra of high-quality GaAs quantum wells always display an excitonic behavior[2,4–7]; yet experimental values of the exciton binding energy itself have rarely been reported. This probably arises from a lack of certainty in determining the needed free-electron (hole) energy levels for these structures. The only value available in the literature, to our knowledge, has been provided by Vojak *et al.*[7] For $L=120$ Å, they found 20 (13) meV for the electron–heavy (light) -hole exciton binding energies which were reported to be in close agreement with the two-dimensional limit. In view of their values of L/a_∞ (1 and 0.7, respectively), this apparently does not seem to be the case, according to Fig. 2.

Besides the experimental difficulties of extracting $R^*(L)$, a comparison between theory and experiments is also hampered by the thickness variation of the transverse reduced mass μ which enters the scaling quantities R_∞ and a_∞. In bulk materials there exists a single fourfold-degenerate ground exciton state. Its binding energy is, to a good approximation, obtained by taking[12]

$$\frac{1}{\mu}=\frac{1}{m_e}+\frac{1}{2}\left[\frac{1}{m_{1h}}+\frac{1}{m_{hh}}\right].$$

The fourfold degeneracy is lifted with decreasing L, as the heavy and light holes have different confinement energies. As shown by Nedorezov,[13] the transverse masses of both light- and heavy-hole subbands are also L dependent and, moreover, the subband dispersion relations in the layer plane are no longer quadratic, displaying electronlike segments for the ground well states.

III. EXCITON IN SEMICONDUCTING GaSb-InAs-GaSb HETEROSTRUCTURES

The GaSb valence-band edge lies $\Delta=0.15$ eV above the InAs conduction-band edge. Hence, due to this unique band-edge relationship, the InAs-GaSb superlattices can display either a semiconducting or a semimetallic band structure, depending on the layer thickness.[8] For equal InAs,GaSb thicknesses the transition takes place at an InAs thickness of $L=85$ Å. In the case of the GaSb-InAs-GaSb heterojunction under consideration, shown in Fig. 5, this has been calculated to occur at $L\sim 100$ Å.[14] In contrast to the GaAs case in Fig. 1, the hole motion is no longer quantized along the z direction. The symmetry mismatch between InAs conduction levels and the GaSb hole levels, however, will effectively confine the electrons in the InAs well and the holes in GaSb, as mentioned earlier. We shall adopt the simplifying assumption of complete confinement. The electron–heavy-hole three-dimensional Bohr radius is very large ($\simeq 300$ Å) and, for the InAs thicknesses corresponding to a semiconducting configuration ($L \lesssim 100$ Å), the thin well limit $L/a_\infty \ll 1$ is satisfied. We can therefore use a separable trial wave function to solve the exciton Hamiltonian [Eq. (1)]. Again dropping the plane-wave term corresponding to the in-plane motion of the center of mass, we have used the trial wave function

$$\psi(\rho,z_e,z_h)=N_1\exp(-\rho/\lambda_1)\cos(\pi z_e/L)f(z_h)\,, \tag{9}$$

$$f(z_h)=\begin{cases}(|z_h|-L/2)\exp\left\{-\left[\dfrac{b_h}{2}\left[|z_h|-\dfrac{L}{2}\right]\right]\right\} & \text{if } |z_h|>\dfrac{L}{2}\\ 0 \text{ if } |z_h|<\dfrac{L}{2}\,.\end{cases} \tag{10}$$

where λ_1 and b_h are the variational parameters and N_1 a normalization constant. Note that $f(z_h)$ is the symmetric combination of Fang-Howard wave functions[15] describing the quantized carrier motion in inversion layers. We use it on the present exciton problem since it is expected to describe correctly the hole binding arising from electron-hole interaction and to satisfy properly the boundary conditions at the interfaces. The thickness dependence of the dimensionless exciton binding energy is shown in Fig. 6. It is seen that R^*/R_∞ extrapolates to ~ 0.8 at vanishing L instead of 4 as in the case of GaAs quantum wells. The reason for such a small binding energy is clear: Since electrons and holes are present in different layers, overlapping only at the interfaces where their wave functions vanish, a dramatic decrease in their binding occurs. For $L/a_\infty \gtrsim 0.3$, the heterojunction is in a

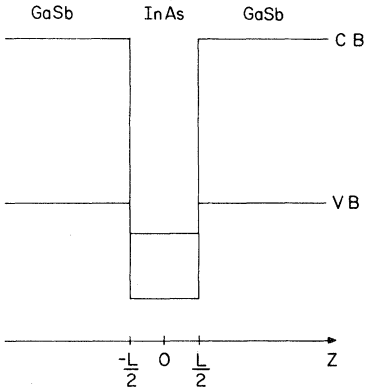

FIG. 5. Energy diagram of the valence (VB) of GaSb and conduction band (CB) of InAs for a GaSb-InAs-GaSb heterostructure.

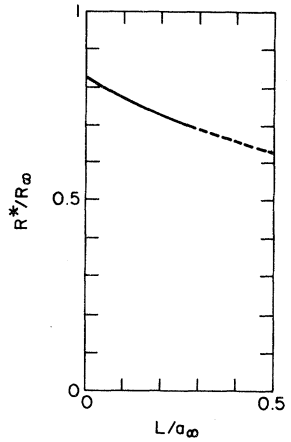

FIG. 6. Dimensionless exciton binding energy R^*/R_∞ is plotted vs the dimensionless InAs thickness L/a_∞ for a GaSb-InAs-GaSb heterostructure. The solid line corresponds to a semiconducting configuration and the dashed line to a semimetallic configuration.

semimetallic configuration and the screening effects, which are not included in our calculations, should further reduce the exciton binding energy with respect to the results shown in Fig. 6.

For electrons and holes moving in separated planes, Lozovik and Nishanov[10] have obtained the two-dimensional value $R^*/R_\infty = 4$ when the distance between planes vanishes. However, in this limit, their configuration resembles the GaAs-GaAlAs case. A rough comparison can still be made between the present results and those obtained for finite separation of planes. To do so, we assimilate the carrier motions to planar ones, taking place on a sheet located at $z=0$ for electrons, and $z = L/2 + 3/b_h$ for holes, where $3/b_h$ is the average value of $(|z_h| - L/2)$ in one of the GaSb layers. For $L = 0.2a_\infty$, we obtain $b_h a_\infty \sim 2$ and $R^* \sim 0.7R_\infty$, which has to be compared with Lozovik and Nishanov's result of $R^* \sim 1.3R_\infty$.

For the experimental superlattice structure of InAs(30 Å)-GaSb(50 Å),[9] we have $L = 30$ Å, $L/a_\infty \sim \frac{1}{10}$ and, according to Fig. 6, $R^* \sim 0.75R_\infty$. Taking for the electron–heavy-hole R_∞ a value of 1.2 meV, we obtain $R^* \sim 0.9$ meV. Such a small binding energy is consistent with the absence of excitonic features in the near-band-gap luminescence spectra.

IV. CONCLUSION

Our variational calculations for the ground exciton binding energy of GaAs-GaAlAs quantum wells show that it decreases monotonically with increasing well thickness, from the two-dimensional ($L=0$) to the three-dimensional ($L=\infty$) Rydberg limits. On the other hand, similar calculations for the InAs-GaSb system indicate that the two-dimensional limit is not recovered at $L=0$, as a consequence of spatial separation of electrons and holes. The resulting small binding energy in this case is consistent with luminescence experiments where excitonic effects were not observed.

The calculations presented are based on simplifying assumptions which we believe do not affect the essential features of the results. The assumption of complete confinement of the carriers in the well could be relaxed which, except for extremely narrow GaAs wells ($L \lesssim 30$ Å), should not change the binding energy appreciably. We have ignored the intricate hole kinematics in the well plane. Taking it into account would greatly complicate the formulation of the exciton problem, which seems hardly justified in view of the scarcity of experimental data.

ACKNOWLEDGMENT

This work was supported in part by the US Army Research Office.

*Permanent address: Groupe de Physique des Solides de l'E.N.S., 24 rue Lhomond 75231 Paris Cedex 05, France.

[1]L. Esaki, and R. Tsu, IBM J. Res. Dev. 14, 61 (1970).

[2]R. Dingle, in *Festkorperprobleme XV (Advances in Solid State Physics)*, edited by H. J. Queisser (Pergamon, Vieweg, Braunschweig, 1975), p. 21.

[3]L. Esaki and L. L. Chang, Thin Solid Films 36, 285 (1976).

[4]C. Weisbuch, R. C. Miller, R. Dingle, A. C. Gossard, and W. Wiegmann, Solid State Commun. 37, 219 (1981).

[5]R. C. Miller, D. A. Kleinman, W. T. Tsang, and A. C. Gossard, Phys. Rev. B 24, 1134 (1981).

[6]R. C. Miller, D. A. Kleinman, W. A. Nordland, Jr., and A. C. Gossard, Phys. Rev. B 22, 863 (1980).

[7]B. A. Vojak, N. Holonyak, Jr., W. D. Laidig, K. Hess, J. J. Coleman, and P. D. Dapkus, Solid State Commun. 35, 477 (1980).

[8]For a recent review, see L. L. Chang, Proceedings of the XVth International Conference on Semiconductors, Kyoto, 1980 [J. Phys. Soc. Jpn. 69, Suppl. A, 997 (1980)].

[9]P. Voisin, G. Bastard, C. E. T. Gonsalves da Silva, M. Voos, L. L. Chang, and L. Esaki, Solid State Commun. 39, 79 (1981).

[10]Y. E. Lozovik and V. N. Nishanov, Fiz. Tverd. Tela. (Leningrad) 18, 3267 (1976) [Sov. Phys.—Solid State 18, 1905 (1976)].

[11]Such a statement arises from the comparison between the calculated binding energy of a hydrogenic donor located at the center of the well assuming (i) perfect confinement: G. Bastard, Phys. Rev. B 24, 4714 (1981); (ii) imperfect confinement: C. Mailhiot, Yia-Chung Chang, and T. C. McGill, Surf. Sci. 113, 161 (1982).

[12]A. Baldereschi and Nunzio C. Lipari, Phys. Rev. B 3, 439 (1971).

[13]S. S. Nedorezov, Fiz. Tverd. Tela. (Leningrad) 12, 2269 (1970) [Sov. Phys.—Solid State 12, 1814 (1971)].

[14]G. Bastard, E. E. Mendez, L. L. Chang, and L. Esaki, in Physics and Chemistry of Solid State Interfaces, Asilomar, 1982 [J. Vac. Sci. Technol. (in press)].

[15]F. F. Fang and W. E. Howard, Phys. Rev. Lett. 16, 797 (1966).