Exciton binding energy in GaAs/$Al_xGa_{1-x}As$ multiple quantum wells

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We have used a variational three-dimensional trial envelope function to calculate the exciton binding energy in GaAs/$Al_xGa_{1-x}As$ multiple quantum wells. In all the limiting cases that the barrier width $d_A \to \infty$ or $d_A \to 0$, and the well width $d_B \to \infty$ or $d_B \to 0$, the calculated binding energy approaches the respective correct value. From the computed binding energies in several experimentally studied samples, we have discovered the systematic dependence of the exciton binding energy on the well width and the barrier width.

The fabrication of high-quality semiconductor heterostructures and multiple quantum wells (MQW's) allows the study of the quantum size effect[1,2] in the physical properties of these systems, which are quite different from those of the corresponding bulk materials. The subband formation strongly influences the exciton effects, which dominate the optical absorption and the photoluminescence spectra of both single GaAs/$Al_xGa_{1-x}As$ quantum wells and GaAs/$Al_xGa_{1-x}As$ MQW's.[3-5] Even at room temperature the sharp exciton lines can be detected in the absorption spectra of GaAs/$Al_xGa_{1-x}As$ MQW's,[6] but can hardly be observed in bulk GaAs samples. In connection with the possible applications to integrated optics,[7] such materials have been recently investigated extensively.

Both the variational method[8-11] and the perturbation theory[12] have been commonly used to study the exciton in MQW's, besides the **k**-space approach of Broido *et al.*[13] and the self-consistent numerical scheme proposed by Wu.[14] In this Brief Report we will use a variational three-dimensional envelope function to obtain the exciton binding energy E_b in GaAs/$Al_xGa_{1-x}As$ MQW's. The computed E_b approaches the correct limiting binding energy of an exciton in a single quantum well.[15,16] Our calculation also reveals a systematic dependence of the exciton binding energy on the well width and the barrier width.

We will first outline the relevant theoretical analysis and computation scheme for excitons in a MQW, the details of which can be found in the literature.[10,12,17] In the effective-mass approximation, we need to solve the Schrödinger equation along the z axis which is perpendicular to the interfaces. The corresponding Hamiltonian is

$$H_\zeta = \frac{-\hbar^2}{2}[m_\zeta(z_\zeta)]^\alpha \frac{d}{dz}[m_\zeta(z_\zeta)]^\beta \frac{d}{dz}[m_\zeta(z_\zeta)]^\alpha + V_\zeta(z_\zeta), \tag{1}$$

where $2\alpha+\beta=-1$, with $\zeta=e$ for a conduction electron and $\zeta=h$ for a (light or heavy) valence hole. $V_e(z_e)$ and $V_h(z_h)$ are square-well-barrier array type potentials illustrated in Fig. 1 of Ref. 17. The spatial-dependent effective mass $m_\zeta(z_\zeta)$ has the correct bulk value of the barrier material and the well material. Except for the matching parameter β and the band offset Q which appears in $V_\zeta(z_\zeta)$, all material parameters needed to solve (1) are available from existing experimental data. While the early calculation[18] suggested a value $Q \sim 0.9$, the commonly accepted value now[19] is $Q \sim 0.6$–0.65, which is also the conclusion of our recent tight-binding calculation.[20] The procedure of deriving the eigenstates of (1) and the dependence of the subband structure on the values of β were investigated earlier with a numerical computation.[17] In the present work, a similar numerical check on the exciton ground state indicates that the binding energy of the exciton is insensitive to the values of β in the region of $-1<\beta<0$. Therefore, in the rest of this paper we set $\beta=-1$ and $Q=0.65$.

When the Coulomb interaction between the electron and the hole is taken into account, the Hamiltonian of an exciton in a MQW has the form

$$H = H_e + H_h + H_{eh} , \tag{2}$$

where

$$H_{eh} = \frac{-\hbar^2}{2\mu}\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right] - \frac{e^2}{\epsilon|\mathbf{r}_e-\mathbf{r}_h|} . \tag{3}$$

In the above equations, $\mathbf{r}_e=(x_e,y_e,z_e)$ and $\mathbf{r}_h=(x_h,y_h,z_h)$ are the positions of a conduction electron and a valence hole, respectively. μ is the reduced mass of the electron-hole pair, and $(x,y)=(x_e-x_h,y_e-y_h)$ label their relative position in the z-y plane. ϵ is the static dielectric constant, and for the bulk $Al_xGa_{1-x}As$ alloy, $\epsilon(x)=13.18-3.12x$.[21] Since we are interested in the region of small $x<0.4$, it is reasonable to use the averaged value $\sqrt{\epsilon(0)\epsilon(x)}$ for the GaAs/$Al_xGa_{1-x}As$ MQW. In certain cases[13] one simply uses $\epsilon=13.18$.

Let $\psi_e(z_e)$ and $\psi_h(z_h)$ be, respectively, the normalized eigenstates of H_e and H_h. The trial wave function for the exciton ground state can be expressed as

$$\Psi(\mathbf{r}',z_e,z_h)=\psi_e(z_e)\psi_h(z_h)\varphi(\mathbf{r}',z_e,z_n)\ , \tag{4}$$

where $\mathbf{r}'=(x,y)$ is a two-dimensional vector in the x-y plane. The exciton envelope wave function $\varphi(\mathbf{r}',z_e,z_h)$ is approximated by a three-dimensional hydrogenic-type wave function[15]

$$\varphi_{3D}(\mathbf{r}',z_e,z_h) =C_3(1+\chi|z_e-z_h|^2)\times\exp\{-[r'^2+(z_e-z_h)^2]^{1/2}/\lambda\}, \tag{5}$$

where C_3 is the normalization constant. The χ and the Bohr radius λ are variational parameters to be determined from minimizing the total energy $\langle H\rangle$ $=\langle\Psi|H|\Psi\rangle$. The binding energy of an exciton in its ground state is then given by

$$E_b=-(\langle\Psi|H|\Psi\rangle-\langle\psi_e\psi_h|H_e+H_h|\psi_e\psi_h\rangle)\ . \tag{6}$$

The subband Bloch states $\psi_e(z_e)$ and $\psi_h(z_h)$ and subband structures of GaAs/Al_xGa_{1-x}As MQW's with $x<0.4$ were derived in our earlier work.[17] Knowing these Bloch states, E_b is readily calculated. Let d_A be the barrier width and d_B the well width, and so $d=d_A+d_B$ the lattice constant of the MQW. When (2)–(5) are substituted into (6), the exciton binding energy $E_b(\lambda,\chi)$ as a function of the variational parameters λ and χ can be expressed as

$$\begin{aligned}E_b(\lambda,\chi)&=-\langle\psi_e(z_e)\psi_h(z_h)\varphi_{3D}(\mathbf{r}',z_e,z_h)|H_e(z_e)+H_h(z_h)+H_{eh}(\mathbf{r}',z_e,z_h)|\psi_e(z_e)\psi_h(z_h)\varphi_{3D}(\mathbf{r}',z_e,z_h)\rangle\\&\quad+\langle\psi_e(z_e)\psi_h(z_h)|H_e(z_e)+H_h(z_h)|\psi_e(z_e)\psi_h(z_h)\rangle\\&=-\lim_{N\to\infty}\left[\sum_{\eta,\upsilon=1}^{N}\int_{(\eta-1)d}^{\eta d}dz_e\int_{(\upsilon-1)d}^{\upsilon d}dz_h\,G(\lambda,\chi;z_e,z_h)\right],\end{aligned} \tag{7}$$

where $G(\lambda,\chi;z_e,z_h)$ is a complicated function of the positions of electron and hole along the z axis.

Before going further to calculate $E_b(\lambda,\chi)$, it is important to point out the intrinsic deficiency of the use of the two-dimensional exciton envelope wave function

$$\varphi_{2D}(\mathbf{r}')=C_2\exp(-r'/\lambda)\ , \tag{8}$$

where C_2 is a normalization constant. When it is used in (6) the exciton binding energy is reduced to

$$E_b^{2D}(\lambda)=-\lim_{N\to\infty}\left[\sum_{\eta,\upsilon=1}^{N}\int_{(\eta-1)d}^{\eta d}dz_e|\psi_e(z_e)|^2\int_{(\upsilon-1)d}^{\upsilon d}dz_h|\psi_h(z_h)|^2\langle\varphi_{2D}(\mathbf{r}')|H_{eh}(\mathbf{r}',z_e,z_h)|\varphi_{2D}(\mathbf{r}')\rangle\right]. \tag{9}$$

We notice that $\varphi_{2D}(\mathbf{r}')$ does not depend on z_e and z_h. Therefore the matrix element $\langle\varphi_{2D}(\mathbf{r}')|H_{eh}(\mathbf{r}',z_e,z_h)|\varphi_{2D}(\mathbf{r}')\rangle$ decreases with increasing $|z_e-z_h|$. When z_e and z_h are in different quantum wells, the corresponding matrix element has a very small value. If we neglect such small quantities, (9) can be well approximated as

$$E_b^{2D}(\lambda)\approx-\lim_{N\to\infty}\left[N\int_0^d dz_e\int_0^d dz_h|\psi_e(z_e)\psi_h(z_h)|^2\langle\varphi_{2D}(\mathbf{r}')|H_{eh}(\mathbf{r}',z_e,z_h)|\varphi_{2D}(\mathbf{r}')\rangle\right]. \tag{10}$$

Since both $\psi_e(z_e)$ and $\psi_h(z_h)$ are normalized to unity, we have

$$\int_0^d dz_e|\psi_e(z_e)|^2=\int_0^d dz_h|\psi_h(z_h)|^2=\frac{1}{N}\ .$$

Hence the exciton binding energy $E_b^{2D}(\lambda)$ is inversely proportional to N, and approaches zero as N increases to infinity.

The analytical conclusion that $E_b^{2D}(\lambda)\to0$ as $N\to\infty$ has been confirmed by a numerical calculation. Furthermore, if we use the original formulation of Jiang's perturbation calculation[12] of the exciton binding energy, we reach the same conclusion that the exciton binding energy vanishes as $N\to\infty$. These results are the consequence of unphysical choices of the envelope wave function for an exciton in a MQW, which make the exciton delocalize along the z axis.

Now we return to (7) to calculate the exciton binding energy $E_b(\lambda,\chi)$. When the well width d_B is much larger than the Bohr radius λ_0, then the exciton stays in a single well and its physical properties are the same as those of a free exciton in a pure GaAs bulk sample. If d_B is comparable to or less than λ_0, the exciton cannot be confined in a single well unless the barrier width d_A is so large that $d_A+d_B\gg\lambda_0$. Finally, if d_A+d_B is about a few times the Bohr radius λ_0, then the exciton extends over more than a single well. Therefore, to calculate $E_b(\lambda,\chi)$ from (7), the value of N must be sufficiently large in order to ensure a convergent result. Furthermore, since the computation of $E_b(\lambda,\chi)$ involves numerical integration over z_e and z_h, we have taken precautions against the possible numerical inaccuracy which may appear when the domain of integration becomes much larger than the MQW lattice constant $d=d_A+d_B$.

The effective mass of the conduction-band electron at the Γ valley is isotropic and has been determined experimentally[21] as $m_e(x)=(0.067+0.083x)m_0$ (same value for both the density-of-states and the conductivity electron mass). However, since the light- and heavy-hole bands in bulk $Al_xGa_{1-x}As$ with $x<0.38$ are degenerate, the effective masses of the valence-band holes are anisotropic. For a given alloy concentration x, the longitudinal (along

the z axis) heavy- and light-hole effective masses $m_{\mathrm{hh}z}(x)$ and $m_{\mathrm{lh}z}(x)$ are used to solve (1), while the computation of the reduced mass $\mu(x)$ in (3) needs the transverse (parallel to the interfaces) heavy- and light-hole effective masses $m_{\mathrm{hh}t}(x)$ and $m_{\mathrm{lh}t}(x)$. These anisotropic effective masses can hardly be measured by experiments, which usually give an averaged value over the longitudinal and the transverse masses. In our calculation we will determine the hole effective masses from the band-structure parameters.

The degenerate light- and heavy-hole subbands in bulk $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ are calculated from the Luttinger Hamiltonian.[22] At $\mathbf{k}=\mathbf{0}$ the heavy hole and the light hole are decoupled, and the anisotropic hole effective masses are simple functions of the band-structure parameters $\gamma_1(x)$ and $\gamma_2(x)$,[23]

$$\left.\begin{matrix} m_{\mathrm{hh}z}(x) \\ m_{\mathrm{lh}z}(x) \end{matrix}\right\} = -\frac{m_0}{[\pm 2\gamma_2(x)-\gamma_1(x)]} , \tag{11a}$$

$$\left.\begin{matrix} m_{\mathrm{hh}t}(x) \\ m_{\mathrm{lh}t}(x) \end{matrix}\right\} = \frac{m_0}{[\gamma_1(x)\pm\gamma_2(x)]} , \tag{11b}$$

where the + sign is for the heavy holes and the − sign is for the light holes. The band-structure parameters have been calculated by Lawaetz[24] as $\gamma_1(x=0)=7.65$ and $\gamma_2(x=0)=2.41$ for bulk GaAs, and $\gamma_1(x=1)=4.04$ and $\gamma_2(x=1)=0.78$ for bulk AlAs. With the band-structure parameters we will first determine from (11a) and (11b) the effective masses

$$m_{\mathrm{hh}z}(x=0)=0.353m_0,\quad m_{\mathrm{lh}z}(x=0)=0.080m_0 ,$$

$$m_{\mathrm{hh}t}(x=0)=0.099m_0,\quad m_{\mathrm{lh}t}(x=0)=0.191m_0$$

for pure GaAs, and

$$m_{\mathrm{hh}z}(x=1)=0.403m_0,\quad m_{\mathrm{lh}z}(x=1)=0.178m_0 ,$$

$$m_{\mathrm{hh}t}(x=1)=0.207m_0,\quad m_{\mathrm{lh}t}(x=1)=0.307m_0$$

for pure AlAs. Then, we can use the linear interpolation to obtain the hole effective masses for the $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ alloy with $0<x<0.38$. However, owing to the conditions Eqs. (11a) and (11b), we can only linearly interpolate the longitudinal (or transverse) hole masses and from them calculate the transverse (or longitudinal) hole masses via (11a) and (11b). Both ways produce very similar exciton binding energies. Because the longitudinal masses will be used first in deriving the subband structure from (1), we simply linearly interpolate them as $m_{\mathrm{hh}z}(x)=(0.353+0.05x)m_0$ and $m_{\mathrm{lh}z}(x)=(0.08+0.098x)m_0$.

We should point out that the above analysis is valid for $\mathbf{k}=0$ at which the heavy- and light-hole bands are decoupled. Since the exciton is not formed at $\mathbf{k}=0$ alone but rather over a range of $\mathbf{k}$ space, the resultant mixing of the heavy and light hole has been ignored in our calculation.

In the following we present our computed E_b of an exciton consisting of a valence heavy hole and a conduction electron. The binding energy of an exciton which is a bound state of a valence light hole and a conduction electron can be similarly calculated. Since a finite length of N superlattice constants must be used for the z-axis integration in (7), the exciton binding energy so obtained is expressed as $E_{\mathrm{ex},N}$. The nonconverged binding energy $E_{\mathrm{ex},1}$ and the converged binding energy $E_{\mathrm{ex},30}$ of two sets of $\mathrm{GaAs/Al_{0.25}Ga_{0.75}As}$ samples are shown in Fig. 1. These samples have two values of the barrier width $d_A=100$ and 300 Å, but with the well width d_B varying from 10 to 400 Å. We see clearly that for a given value of d_B, the error $E_{\mathrm{ex},1}-E_{\mathrm{ex},30}$ increases with decreasing d_A. For a given value of d_A, the $E_{\mathrm{ex},30}$ curve also approaches

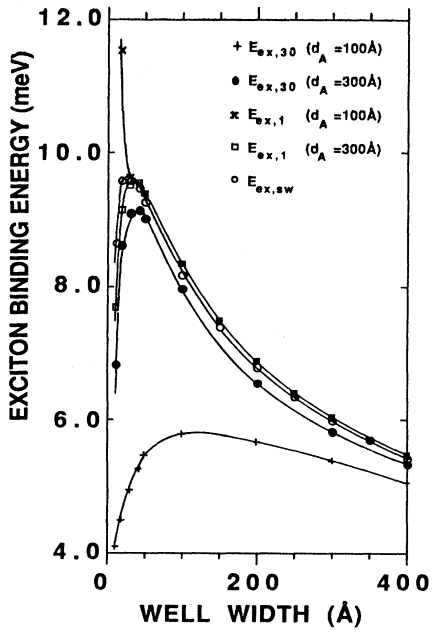

FIG. 1. Ground-state binding energy of a heavy-hole electron exciton for two $\mathrm{GaAs/Al_{0.25}Ga_{0.75}As}$ MQW samples with fixed barrier width $d_A=100$ and 300 Å, and for one $\mathrm{GaAs/Al_{0.25}Ga_{0.75}As}$ single-well sample. For all samples the well width varies from 10 to 400 Å. In the region of well width larger than 50 Å, the × points and the open-square points coincide, resulting in solid-square points.

TABLE I. Ground-state binding energy (meV) of an exciton consisting of a valence-band heavy hole and a conduction-band electron in various *realistic* $\mathrm{GaAs/Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ MQW samples. The rows are ordered with decreasing superlattice constant $d=d_A+d_B$ in order to demonstrate the trend of $\Delta E_{\mathrm{ex}}=E_{\mathrm{ex,SW}}-E_{\mathrm{ex},30}$.

d_A	d_B	x	$E_{\mathrm{ex},30}$	$E_{\mathrm{ex,SW}}$	ΔE_{ex}	d_A+d_B
125	460	0.20	4.96	5.15	0.19	585
260	260	0.28	6.03	6.28	0.25	520
100	315	0.25	5.33	5.89	0.56	415
150	200	0.30	6.15	6.83	0.68	350
100	210	0.25	5.64	6.71	1.07	310
100	150	0.25	5.78	7.40	1.62	250
100	116	0.25	5.80	7.91	2.11	216
19	188	0.30	4.49	6.95	2.46	207
100	90	0.25	5.76	8.38	2.62	190
25	150	0.25	4.43	7.40	2.97	175
25	90	0.25	4.26	8.38	4.12	115

the binding energy of an exciton in a bulk GaAs as $d_B \rightarrow \infty$, and the binding energy of an exciton in a bulk $Al_{0.25}Ga_{0.75}As$ as $d_B \rightarrow 0$.

We have also calculated the binding energy $E_{ex,SW}$ of an exciton in a single quantum well of $GaAs/Al_{0.25}Ga_{0.75}As$ as a function of the well width d_B, which has been investigated earlier.[15,16] $E_{ex,SW}$ is plotted in Fig. 1 as the curve with open circles. The results in Fig. 1 demonstrate correctly the tendency $E_{ex,30} \rightarrow E_{ex,SW}$ as the barrier width $d_A \rightarrow \infty$. It is worthwhile to point out that if we use the band offset $Q = 0.85$ and the set of material parameter values specified in the paper of Greene and Bajaj,[15] our calculated $E_{ex,SW}$ reproduces the exciton binding-energy curve given in Fig. 1 of Ref. 15.

Finally, we calculated the exciton binding energies of many MQW samples which were studied experimentally with optical measurements.[3,4,25–27] The results are listed in Table I, with ΔE_{ex} defined as the energy difference $\Delta E_{ex} = E_{ex,SW} - E_{ex,30}$. The rows in Table I are ordered with increasing superlattice constant $d = d_A + d_B$. It is important to point out that although the *realistic samples* in Table I have various thicknesses (d_A and d_B) and Al concentration (x), the energy difference ΔE_{ex} increases monotonically when the superlattice constant $d = d_A + d_B$ is reduced.

To close this Brief Report, we should mention that for most samples studied in Fig. 1 and Table I, the effective Bohr radius a_0^* in the envelope function has its optimal value around 100 to 180 Å. Hence, when the superlattice constant d is comparable to a_0^*, a substantial fraction of the exciton binding energy is due to the interaction between the electron in one well and the hole in another well (especially in an adjacent well). When $d \approx a_0^*$, we found a large contribution of about 3–4 meV from these interwell terms. In the binding energy $E_{ex,SW}$, there is no such interwell contribution.

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