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LETTER TO THE EDITOR

Binding and overlap function of incompletely confined excitons in quantum dots

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Abstract. Using a variational method with introduction of effective electron potentials, binding energies and overlap functions of exciton ground states in ZnSe/ZnS quantum dots (QDs) with small conduction-band offset are calculated. It is found that excitons in ZnSe/ZnS QDs are incompletely confined due to the extension of electrons in the weak confinement condition. The binding energies of such excitons are almost independent of potential shapes and quantum sizes while the overlap functions are dependent on the shapes and sizes of QDs. It is quite different between ZnSe/ZnS and conventional QDs and this will be subjected to experimental verification in the future.

Recently, advances in fabrication technology have made it possible to manufacture semiconductor quantum dots (QDs) in which the motion of electron and hole carriers or that of one kind of carrier is strongly confined in all three spatial dimensions. This can be achieved using a variety of techniques. For example, extensive efforts on III–V materials such as InAs/GaAs [1–2] have demonstrated that self-organized QDs can be directly fabricated by molecular beam epitaxy utilizing the Stranski–Krastnow mechanism. The self-organization process can also be realized in the case of II–VI materials such as CdSe/ZnSe [3–5].

The quantum confinement, under which the motion of electrons and holes is mainly in the regions of the deep confining potentials induced by band offsets, has been observed in both III–V [6–8] and II–VI [4, 5, 9] quantum dots even though the structures characterized by length scales for exciton localization are quite different from each other. In some QDs such as ZnSe/ZnS QDs, however, the motion of only one kind of carrier is strongly confined in all three spatial dimensions so that the excitons are not strongly confined as conventional ones are. What about the quantum confinement effect and character of exciton states in such QDs? To our knowledge, there have been no reports on the problem in either experimental observations or theoretical investigations. In order to show the character of incompletely confined excitons in QDs, we have for the first time studied the binding energies and overlap functions of exciton states in ZnSe/ZnS quantum dots with small conduction-band offset [10, 11] i.e. with only holes confined strongly, in this letter.

Within the framework of an effective-mass approximation, the Hamiltonian of an electron (a hole) of a spherical quantum dot can be written as

$$H_i = -\frac{\hbar^2 \nabla_i^2}{2m_i} + V_i(r_i) \tag{1}$$

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where m_i is effective mass, and $i = e$ and $i = h$ correspond to electron and hole, respectively. The potential $V_i(r)$ is taken to be spherically symmetric in the present work and has the form

$$V_i(r) = \begin{cases} V_{i0} & \text{if } r \geqslant R_0 \\ \alpha r^k & \text{if } r < R_0 \end{cases} \tag{2}$$

where V_{i0} is the barrier height and can be obtained from a fixed ratio Q_i of the band-gap discontinuity ΔE_g between ZnSe and ZnS i.e. $V_{i0} = Q_i \Delta E_g$. α is equal to V_{i0}/R_0^k. R_0 is the radius of the quantum dot. The shape of $V_i(r)$ is determined by k.

The Hamiltonian of an exciton in the dot is as follows:

$$H = H_e + H_h - \frac{e^2}{\epsilon r_{eh}} \tag{3}$$

where the last term is the Coulomb interaction between the electron and the hole. We have neglected the effect of heavy-hole–light-hole mixing here. It is interesting to point out that the quantum confinement of electrons and holes in conventional QDs is much stronger than that induced by the Coulomb interaction. In ZnSe/ZnS QDs formed by self-organized growth, however, electrons are weakly confined by the $V_e(r_e)$ because Q_e is very small. In fact, there is no electron bound state in $V_e(r_e)$ as R_0 is less than the electron confinment radius R_{ec}, which is related to V_{e0} and k of equation (2). For $k = \infty$, for example, $R_{ec} = 1.11\hbar/(V_{e0}m_e)^{1/2}$. For a fixed V_{e0}, the R_{ec} decreases with increasing k. In the present study, the R_0 of ZnSe/ZnS QDs is less than or close to R_{ec}. Hence the coupling between $V_e(r_e)$ and electron–hole interaction plays an important role in bounding electrons and forming excitons and has a strong influence on the binding energies in ZnSe/ZnS QDs.

A suitable approximation method should be established to treat the electron-hole interaction for obtaining the electron and then exciton wavefunctions and binding energies correctly. To solve the problem, we start with equation (3), which can be rewritten as

$$H = H_{eff,e}(A, B) + H_h + H'(A, B) \tag{4}$$

with

$$H_{eff,e}(A, B) = H_e + W(r_e, A, B) \tag{5}$$

and

$$H'(A, B) = -\frac{e^2}{\epsilon r_{eh}} - W(r_e, A, B) \tag{6}$$

where $W(r_e, A, B)$ represents an effective electron potential introduced by a confined hole in the dot. It is interesting to note that the hole is mainly confined by the dot in the regime of R_0. Therefore the form of the effective potential W can be quite different in different regimes of r_e. According to the difference, it is reasonable to take W as the following:

$$W(r_e, A, B) = \begin{cases} Ar_e^2 - B & \text{if } r_e \leqslant R_\alpha \\ A_m r_e^2 - B_m - \frac{e^2}{\epsilon r_e} & \text{if } R_\alpha < r_e \leqslant R_\beta \\ -\frac{e^2}{\epsilon r_e} & \text{if } R_\beta < r_e < \infty. \end{cases} \tag{7}$$

Here we have introduced two parameters A and B to be determined by a variational principle. A_m and B_m can be deduced from A and B by using the continuity of W at the interface $r_e = R_\alpha$ and $r_e = R_\beta$ where the ratios of R_α and R_β to R_0 are chosen and then fixed. The total process can make the variational calculation more effective. At the same time, a quite reasonable potential W is obtained.

Now, we can exactly solve the Schrödinger-like equations with spherically symmetric potentials

$$H_{eff,e}(A, B)[R_{nl}(r_e, A, B)Y_{lm}(\theta_e, \varphi_e)] = E_{e,nl}(A, B)[R_{nl}(r_e, A, B)Y_{lm}(\theta_e, \varphi_e)] \tag{8}$$

and

$$H_h[R_{kl}(r_h)Y_{lm}(\theta_h, \varphi_h)] = E_{h,kl}[R_{kl}(r_h)Y_{lm}(\theta_h, \varphi_h)] \tag{9}$$

where $n(k), l$ and m are the principal, orbital and magnetic quantum numbers, respectively. Then all of the exact eigenenergies and the corresponding eigenfunctions, which are in different forms of series expansion in different regions of the radial equations, are obtained [12]. Using the exact eigenfunctions given above, we can easily construct the trial functions of the exciton ground state

$$\Psi_0(r_e, r_h, A, B) = R_{10}(r_e, A, B)R_{10}(r_h) \tag{10}$$

which is normalized. Thus the ground-state energy E_G is given by the variational calculation

$$E_G = \min_{A,B}\langle R_{10}(r_e, A, B)R_{10}(r_h)|H|R_{10}(r_e, A, B)R_{10}(r_h)\rangle. \tag{11}$$

Assuming that E_G approaches the minimum at $A = A_f$ and $B = B_f$, we can obtain

$$E_G = E_{h,10} + E_{e,10}(A_f, B_f) + E'(A_f, B_f) \tag{12}$$

with

$$E'(A_f, B_f) = \langle R_{10}(r_e, A_f, B_f)R_{10}(r_h)|H'(A_f, B_f)|R_{10}(r_e, A_f, B_f)R_{10}(r_h)\rangle. \tag{13}$$

Substituting equations (6) and (10) into equation (13), we can find $E'(A_f, B_f)$ in the form

$$\begin{aligned} E'(A_f, B_f) = &-\int_0^\infty R_{10}(r_e, A_f, B_f)W(r_e, A_f, B_f)R_{10}(r_e, A_f, B_f)r_e^2\mathrm{d}r_e \\ &-\Big[\int_0^\infty R_{10}(r_h)R_{10}(r_h)r_h^2\mathrm{d}r_h\Big[\int_0^{r_h} R_{10}(r_e, A_f, B_f)R_{10}(r_e, A_f, B_f)\frac{r_e^2}{r_h}\mathrm{d}r_e \\ &+\int_{r_h}^\infty R_{10}(r_e, A_f, B_f)R_{10}(r_e, A_f, B_f)r_e\mathrm{d}r_e\Big]\Big]. \end{aligned} \tag{14}$$

Compared with the cases in one, two, and three dimensions, the binding energy is defined by

$$E_B = E_0 - E_G = E_{e,0} - E_{e,10}(A_f, B_f) - E'(A_f, B_f) \tag{15}$$

where E_0 and $E_{e,0}$ are respectively the exciton and electron ground-state energies in the absence of the hole–electron interaction. $E_{e,10}(A_f, B_f)$ is the lowest eigenenergy of $H_{eff,e}(A_f, B_f)$. Further, according to the absolute values of $E'(A_f, B_f)$, we can gauge whether the $W(r_e, A_f, B_f)$ is suitable for describing the coupling between $V_e(r_e)$ and the electron–hole interaction mentioned above. Compared with E_B, the less $|E'(A_f, B_f)|$ is, the better $W(r_e, A_f, B_f)$ is. Once the E_G is known, the overlap function

$$I_G = \Big|\int R_{10}(r, A_f, B_f)R_{10}(r)r^2\mathrm{d}r\Big|^2 \tag{16}$$

related to the oscillation strength, can be easily obtained.

For the self-organized QDs, both of R_0 and V_{e0} depend on the growth conditions. We assume that for ZnSe/ZnS QDs, the R_0 is between 22 and 34 Å and V_{e0} is about 32 meV and that the potential is usually deviated from the square ($k = \infty$) one. For a better understanding, we have calculated ground states of excitons in ZnSe/ZnS QDs of $V_{h0} = 860$ meV as a function of k, R_0 and V_{e0}, respectively. In calculations, we take

$m_e = 0.16m_0$ (m_0 is the free electron mass), $m_h = 0.61m_0$ and $\epsilon = 8.7$ for ZnSe and $m_e = 0.27m_0$, $m_h = 0.96m_0$ and $\epsilon = 8.1$ for ZnS, respectively.

In table 1, E_G, E_B and I_G have been shown for excitons in QDs of $k = \infty$ with $V_{e0} = 3279$ ($V_{h0}m_h/m_e$), 88 and 32 meV and $R_0 = 22, 25, 34, 42$ and 56 Å, respectively. We should note that the variation of E_B and I_G with R_0 is quite different between the two cases of $V_{e0} = V_{h0}m_h/m_e$ and 32 meV. As shown in the table, the E_B of $V_{e0} = V_{h0}m_h/m_e$ strongly increases with decreasing R_0 while that of $V_{e0} = 32$ meV is found to be almost constant around 45 meV in the region of R_0 between 22 and 42 Å. I_G of $V_{e0} = V_{h0}m_h/m_e$ is equal to 1 while that of $V_{e0} = 32$ meV is less than 1 and increases with R_0. These results mean that with increasing R_0, the oscillator strength of a completely confined exciton decreases while that of an incompletely exciton can increases. The values of E_B and I_G are larger for $V_{e0} = V_{h0}m_h/m_e$ than for $V_{e0} = 32$ meV and both E_B values are much larger than the bulk value. It is clearly seen that E_B and I_G are sensitive to V_{e0}; compare those of $V_{e0} = 32$ meV with those of $V_{e0} = 88$ meV.

Table 1. E_G, E_B and I_G of excitons in QDs with $k = \infty$ as a function of V_{e0} and R_0. The energy unit is meV. Taking $m_e = 0.16m_0$ and $m_h = 0.61m_0$, $V_h m_h/m_e = 3279$ meV.

	$V_{e0} = 32$ meV			$V_{e0} = 88$ meV			$V_{e0} = 3279$ meV		
	E_G	E_B	I_G	E_G	E_B	I_G	E_G	E_B	I_G
$R_0 = 22$ Å	74.22	44.57	0.361	105.2	68.04	0.536	242.7	114.7	1.00
$R_0 = 25$ Å	57.85	44.80	0.410	84.89	67.59	0.596	194.3	103.9	1.00
$R_0 = 34$ Å	28.67	45.44	0.535	46.58	60.64	0.721	100.1	81.21	1.00
$R_0 = 42$ Å	13.82	45.52	0.630	25.78	53.19	0.800	55.33	66.89	1.00
$R_0 = 56$ Å	1.524	38.29	0.742	8.217	43.76	0.880	9.523	51.99	1.00

The real m_h is anisotropic for both ZnSe and ZnS materials so we take m_h of ZnSe (ZnS) to be $m_h = m_{hxy} = 0.17$ $(0.31)m_0$ instead of $m_h = m_{hz} = 0.61$ $(0.96)m_0$ to see the anisotropic effect on E_B and I_G of $V_{e0} = 32$ meV. It is found that the effect can be neglected in the incompletely confined excitons because the holes are confined strongly in a small region. Also it is easy to understand that the binding energy of an incompletely confined exciton approaches that (28.8 meV) of a shallow donor in the bulk materials as $V_{h0} \to \infty$, $V_{e0} \to 0$ and $R_0 \to 0$.

In table 2, E_B have been shown for excitons in QDs of $V_{e0} = 32$ meV with $k = 2, 4, 8$ and ∞ and $R_0 = 22, 25, 34, 42$ and 56 Å, respectively. The E_B is also found to be almost constant in the regions of R_0 between 22 and 42 Å with $k = 4, 8$ and ∞ even though E_G values are quite different from each other. This means that the E_B of incompletely confined excitons are almost independent of R_0, and k in the region of R_0.

Table 2. E_B of excitons in QDs with $V_{e0} = 32$ meV as a function of R_0 and k. The energy unit is meV.

	$R_0 = 22$ Å	$R_0 = 25$ Å	$R_0 = 34$ Å	$R_0 = 42$ Å	$R_0 = 56$ Å
$k = 2$	41.92	41.76	41.43	41.52	41.99
$k = 4$	43.08	43.15	43.37	43.89	42.61
$k = 8$	43.80	43.91	44.37	44.61	41.87
$k = \infty$	44.57	44.80	45.44	45.52	38.29

The different characteristics of E_B and I_G between incompletely and completely confined excitons can be explained by noting the difference of the wave functions. For $V_{e0} = 32$ meV, the $R_{10}(r_e, A_f, B_f)$ is much more extended than $R_{10}(r_h)$, which is changed with R_0 and confined mainly within the region of R_0. The binding energies can be almost constant because the extension of electrons and the strong confinement of holes make the hole–electron interaction slightly changed with R_0, m_h and k in the incompletely confined region. I_G is less unity because of the difference between electron and hole wavefunctions. For $V_{e0} = V_{h0}m_h/m_e$, both electron and hole wavefunctions change with R_0 in the same ratio and the interaction increases with decreasing R_0. In fact, the interaction is almost in proportion to $1/R_0$ in conventional QDs both electrons and holes confined strongly. Mentioned above is the reason why there is a such difference.

It is interesting to point out that the ratio of $|E'(A_f, B_f)|$ to E_B is between 0.05 and 0.1. This means that the effective potential $W(r_e, A_f, B_f)$ is suitable for describing the coupling between $V_e(r_e)$ and the electron–hole interaction in the incompletely confined exciton system.

In summary, using the variational method with introduction of effective electron potentials, we have calculated the binding energies and overlap functions of excitons in ZnSe/ZnS quantum dots with small conduction-band offset. The character of completely confined excitons in QDs has been also studied by using $V_{e0} = V_{h0}m_h/m_e$ instead of $V_{e0} = 32$ meV. The two cases are quite different. It has been found that the coupling between the Coulomb and confinement interactions is very important and the binding energies are almost independent of the sizes and shape of QDs for the incompletely confined excitons. However the values are still much larger than those of the bulk materials. Finally, it is interesting to point out that the incompletely confined excitons can exist not only in QDs but also in quantum wells and wires. This will be subjected to experimental verification in the future. Furthermore, we should point out that our method shown here is also suitable for studying the system mentioned above and others, for example, spectra of incompletely confined excitons in different quantum-well structures.

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