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CONFINED EXCITONS, TRIONS AND BIEXCITONS IN SEMICONDUCTOR MICROCRYSTALS

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The dependencies of excitons, trions and biexcitons energy spectra and their oscillator strength on microcrystal radius have been investigated. The calculation taking into account the degeneracy of the valence band has been performed into two limit cases: the small and the large value of the valence band spin-orbit splitting. The total energy of two confined excitons have been shown to be smaller than the energy of confined biexciton in the small size microcrystals which means the negative biexciton bound energy. In the case of the small spin-orbit splitting the all confined exciton complexes are shown to be optical nonactive which explains low quantum efficiency of small size CdS microcrystals.

1.Optical properties of semiconductor microcrystals have been a subject of extensive investigation in recent years [1-6]. The properties were shown to be determined by the energy spectrum of confined electron-hole pairs: the linear optical properties are determined by the one pair (exciton) [2,7], but nonlinear ones by the three charge particles or two of them (trion or biexciton) [8]. The previous calculations of confined exciton energy spectra didn't take into account the degeneracy of valence band [9,7,10].

In the present paper we investigate the influence of the valence band degeneracy on the energy spectrum and oscillator strength of confined excitons, trions and biexcitons. The energy spectra of confined trions and biexcitons wasn't calculated earlier.

2.We consider semiconductors with the cubic-symmetry lattice which valence band edge is described by the Bloch functions of Γ_7 and Γ_8 symmetry. In these semiconductors an electron mass m_e is much smaller then a heavy hole mass m_h and is of the order of a light hole mass m_l: $m_e \sim m_l$, $m_e \ll m_h$. We will consider here two limit values of valence band spin-orbit splitting Δ: the large Δ when hole is described by the four-band Luttinger Hamiltonian $\hat{H}_L^4$ and small Δ ($\Delta = 0$) when hole is described by the three-band Luttinger Hamiltonian $\hat{H}_L^3$ [11]. We shall assume that the microcrystals have a spherical surface with radius a. The wave functions of electrons and holes vanish on this surface which correspond to an infinitely high potential wall surrounding this sphere.

We shall consider here only the case of the strong confinement when microcrystal radius a is smaller then the Bohr radius of electron $a_e = x h^2/m_e e^2$, where x is dielectric coefficient of semiconductor and e is electron charge. Under this condition the energy spectrum of the exciton complexes in microcrystals differs considerably from the bulk one what reveals in the absorption spectra [2]. In this case the size-quantization energy of electron $E_q = h^2\pi^2/2m_e a^2$ is much higher than the energy of interparticle Coulomb interaction in microcrystals which is of the order of e^2/xa. The Coulomb potential of the electrons which affects the holes can be considered then using the condition $m_e \ll m_h$ in adiabatic approximation [9]. This potential has a spherical form:

$$V(r_h) = -\frac{e^2}{x}\int d^3r \frac{\Psi_e^2(r)}{|r_h - r|} \qquad (1)$$

where $\Psi_e = \frac{1}{\sqrt{2\pi a}}\sin(\pi r/a)/r$ is the wave function of the lowest electron quantum-size level.

3. We shall firstly consider the energy spectrum of confined exciton in the case $\Delta \to \infty$ .The adiabatic equation for wave function of such exciton has the form:

$$\hat{H}_0^4\Psi = [\hat{H}_L^4 + V(r)]\Psi = E\,\Psi \qquad (2)$$

with the boundary condition $\Psi(a)=0$. In this case the hole ground state is characterized by the total momentum F=3/2 and is four-fold degenerate with the respect to momentum projection M=±3/2, ±1/2. The wave functions corresponding to these states are [12]

$$\Psi_M = \sum_{l=0,2} R_l(r) \sum_{m+\mu=M} \begin{pmatrix} 3/2 & l & 3/2 \\ \mu & m & -M \end{pmatrix} Y_{l,m} u_\mu \qquad (3)$$

where u_μ are the Bloch functions of the four-fold degenerate valence band Γ_8 ($\mu=\pm1/2,\pm3/2$), $Y_{l,m}$ are the normalized spherical functions, $\begin{pmatrix} i & k & l \\ m & n & p \end{pmatrix}$ are the 3j Wigner symbols, $R_{0,2}$ are the radial functions satisfied the set of second order differential equations [12]. The relationship between these two functions in the limit $m_l/m_h \ll 1$ is [15]:

$$dR_0/dr + (3/r + d/dr)R_2 = 0 \qquad (4)$$

The analytical form of R_0 and R_2 can be obtained in frames of the perturbation theory if $a < a_B = \varkappa\hbar^2/m_h e^2$, what corresponds to the the case of the strong hole size quantization. In the limit $m_l/m_h \ll 1$ we have:

$$R_0 = C[j_0(\varphi_2 r/a) - j_0(\varphi_2)]$$
$$R_2 = C j_2(\varphi_2 r/a) \qquad (5)$$

where j_l are the spherical Bessel functions, $\varphi_2 \approx 5.76$ is the first root of j_2 and $C \approx 6.044/a^{3/2}$ is determined by normalizing: $\int dr r^2 (R_0^2 + R_2^2) = 1$. The ground state energy of such exciton is

$$E_{ex} = \hbar^2\varphi_2^2/(2m_h a^2) - 1.748\, e^2/(\varkappa a) \qquad (6)$$

This energy is measured from the lowest quantum-size level of electron. For obtaining the exciton energy at arbitrary relation between a_B and a we perform the variational calculation. The trial functions for R_0 and R_2 were chosen accounting to an effect of the hole localization in potential (1) [2] and relationship (4):

$$R_2 = C\exp(-\alpha r^2/L^2)\, j_2(\varphi_2 r/a);$$
$$R_0 = -R_2 + 3\int_r^a dr' R_2(r')/r'; \qquad (7)$$

where $L^2 = a^2\sqrt{3\hbar^2\varkappa/2\pi e^2 m_h a}$ and α is dimensionless variational parameter. The variational dependence of E_{ex}/E_B on a is shown in Fig.1 ($E_B = e^2/2\varkappa a_B$). This dependence is in a good agreement with Eq.6 for $a < 20a_B$. Parameter α tends to zero in the same region of a.

We shall now consider an exciton complex consisted of two holes and electron, so called trion. The trions originate as a result of one photon absorption by the ionized microcrystals [8]. In the adiabatic approximation trion is described by the Hamiltonian :

$$\hat{H}_{tr} = \hat{H}_0^4(r_1) + \hat{H}_0^4(r_2) + \frac{e^2}{|r_1 - r_2|} \qquad (8)$$

where r_1 and r_2 are the hole coordinates. The ground state of this Hamiltonian will be found by the

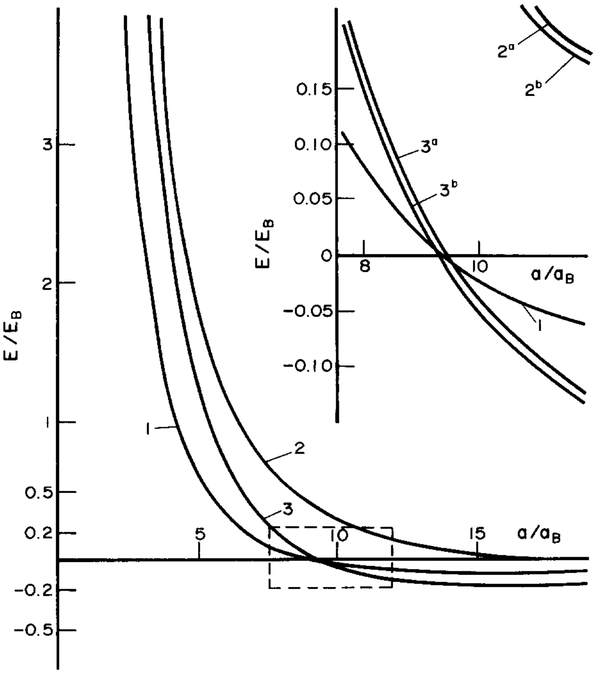

Fig.1 The exciton E_{ex}, trion E_{tr} and biexciton E_{bi} bound energy dependencies on microcrystal radius a in semiconductor with four-fold degenerate valence band. 1 – E_{ex}; 2a, 2b – $E_{tr}(J)$ with J=0,2; 3a, 3b – $E_{bi}(J)$ with J=0,2.The insert: the dependencies on a larger scale.

variational method assuming that the holes with momentum F=3/2 provide the main contribution in the confined trion bound energy. The wave functions of the holes are described by Eq.3. These holes can form two types of trions corresponding to the interchanging antisymmetry condition for two holes wave function. One of them has total momentum J=2 and the other J=0. The wave functions of these states are

$$\Phi^{1,2}_{J,J_z}(r_1,r_2)= \tag{9}$$

$$=(-)^{J_z}\sqrt{2J+1}\sum_{M_1+M_2=J_z}\begin{pmatrix}3/2 & 3/2 & J\\ M_1 & M_2 & -J_z\end{pmatrix}\Psi^1_{M_1}(r_1)\Psi^2_{M_2}(r_2)$$

where J_z is the projection of the momentum J. Here upper index in Ψ_M is introduced for possibility to describe two Ψ_M differed by the parameter α (α_1 and α_2) included into radial functions(R_0^1,R_2^1 and R_0^2,R_2^2). In that case a trial two-particle function have to be taken in the form of antisymmetric sum of the total momentum J eigenfunctions:

$$\zeta_{J,J_z}=\frac{1}{2}\{\Phi^{1,2}_{J,J_z}(r_1,r_2)-\Phi^{1,2}_{J,J_z}(r_2,r_1)\} \tag{10}$$

where J=0,2.The energy of confined trion is easily obtained by the perturbation theory using for R_0 and R_2 Eq.5 if $a < a_B$

$$E_{tr}(J)=2E_{ex}+(1.793-0.024J)e^2/xa \tag{11}$$

Here as in Eq.6 the energy is measured from the energy of lowest quantum-size level of electron E_q. The results of variational two parameter calculation $E_{tr}(J)$ using trial function (10) are shown in Fig.1. It is also well described by Eq.11 for all $a < 20a_B$.

Let us consider now the biexciton using the adiabatic method developed above for trion. The difference is in the doubling of adiabatic potential (1) because the last one is produced by the two electrons. Besides it is necessary to take into account the repulsive energy of two electrons at the first quantum-size level which is equal $1.786e^2/xa$. As a result we obtain the biexciton energy in the case of strong size quantization(a_B>a)

$$E_{bi}(J)=2\left[\frac{h^2\varphi_2^2}{2m_h a^2}-(1.706+0.012J)\frac{e^2}{xa}\right] \tag{12}$$

Here energy is scaled from the total energy of two electrons at the lowest quantum-size level $2E_q$. The biexciton energy is larger then the doubled energy of the exciton what means the negative biexciton bound energy. The same result was obtained by the variational computation using two parameter trial function (10) (see Fig.1).

4. We shall now discuss the oscillator strength of the exciton complexes considered above. It is mainly determined by the square of electron and hole wave functions overlap integral f. For exciton it has the form:

$$f=\left|\int d^3r\ \Psi_{ex}(r,r)\right|^2 \tag{13}$$

where $\Psi_{ex}(r_e,r_h)=\Psi_e(r_e)\Psi(r_h)$ is the confined exciton wave function in adiabatic approximation. For biexciton and trion f is determined as

$$f_{tr,bi}= \tag{14}$$

$$=\left|\int\Psi^*_M(r_h)\zeta^{tr,bi}_{J,J_z}(r_e,r_h)\Psi_e(r_e)d^3r_e d^3r_h\right|^2$$

The holes identity leads to the doubling of f_{tr} and the one more doubling of f_{bi} is due to the electron identity. In this paper we wouldn't consider the peculiarity selection rules of such confined system and the relative values of their oscillator strength. We would investigate only the dependence of Eqs.13,14 on the microcrystal radius.

In the case of strong size quantization the square of the overlap integral can be obtained analytically. Using Eq.5 we obtain for $f=f_{tr}=f_{bi}\approx 0.111$ which is much smaller then the values for semiconductor with the parabolic nondegenerate valence band ($f=f_{tr}=f_{bi}=1$). The results of f, f_{tr} and f_{bi} calculation using the variational functions at arbitrary a are presented in Fig.2. The square of integrals is seen to be practically independent of a and coincide with its limit value 0.111 what means a free character of hole movement. The decrease of f and f_{bi} reflects a certain extent of hole localization in potential (1) which is not a case for trions.

5. We shall now consider the case Δ=0. The hole Hamiltonian of such confined exciton has a form

$$\hat{H}_0^3=\hat{H}_L^3+V(r) \tag{15}$$

The ground state of the hole is characterized by the total momentum F=1 and has three-fold degeneracy with the respect to momentum projection M=0,±1 (the spin degeneracy is neglected). Corresponding wave functions can be written as:

$$\Psi_M=\sum_{l=0}^{2}R_l(r)\sum_{m=-1}^{1}Y_{l,M,m}(\Omega)u_m, \tag{16}$$

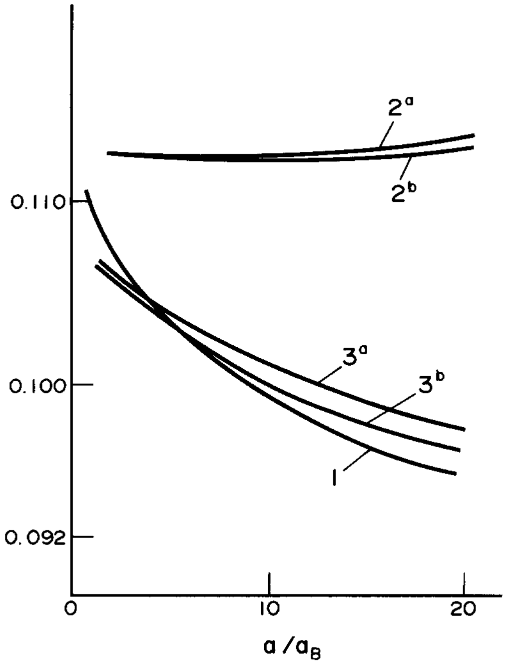

Fig.2 The dependence of the overlap integral square on microcrystal radius a for exciton f – 1; trion $f_{tr}(0)$ – 2a, $f_{tr}(2)$ – 2b; and biexciton $f_{bi}(0)$ – 3a, $f_{bi}(2)$ – 3b.

where u_m are the Bloch function of the three-fold degenerate valence band (the spin component is omitted), $Y_{1,M,m}$ are the components of spherical vector $Y_{1,M}$ [14]. Two solutions of Hamiltonian (15) with different parity are for each F and M. The radial functions of the even solution R_0 and R_2 are satisfied the set of second order differential equations which is similar to one from paper [12] obtained for the four-fold degenerate valence band. But the ground state is formed by the odd solution (16) with radial function R_1 satisfied an equation:

$$\frac{\hbar^2}{2m_h}\left(\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} - \frac{2}{r^2}\right)R_1+(E - V)R_1=0 \quad (17)$$

It is conventional radial Shredinger equation for particles with orbital momentum l=1. In the limit $a \ll a_B$ the solution of Eq.17 satisfying the boundary condition $\Psi_M(a)=0$ is

$$R_1^-(r)=C^- j_1(\varphi_1 r/a), \quad (18)$$

where $\varphi_1 \approx 4.49$ is the first root of the spherical Bessel function j_1 and $C^-=6.51/a^{3/2}$ is the normalizing factor. The energy of such odd exciton state is

$$E_{ex}^-=\hbar^2\varphi_1{}^2/(2m_h a^2)-1.619e^2/(\varkappa a) \quad (19)$$

Under the condition $a \ll a_B$ the lowest eigenstate energy of the even solution E_{ex}^+ is

$$E_{ex}^+=\hbar^2\varphi_2{}^2/(2m_h a^2)-1.827e^2/(\varkappa a) \quad (20)$$

The energy of the odd state E_{ex}^- is smaller then the even state energy E_{ex}^+ for semiconductor with $\Delta=0$ in the case of the strong confinement as it is seen from Eqs.19,20. The same result was obtained by the variational calculation at arbitrary ratio of a and a_B. For odd state we used the trial function

$$R_1^-=C^-\exp(-\alpha r^2/L^2)j_1(\varphi_1 r/a) \quad (21)$$

For even state R_0^+ and R_2^+ are different from Eq.7 by factor $\sqrt{2}$ in R_0 determination: $R_0^+=R_0\sqrt{2}$. The results shown in Fig.3 prove that the odd

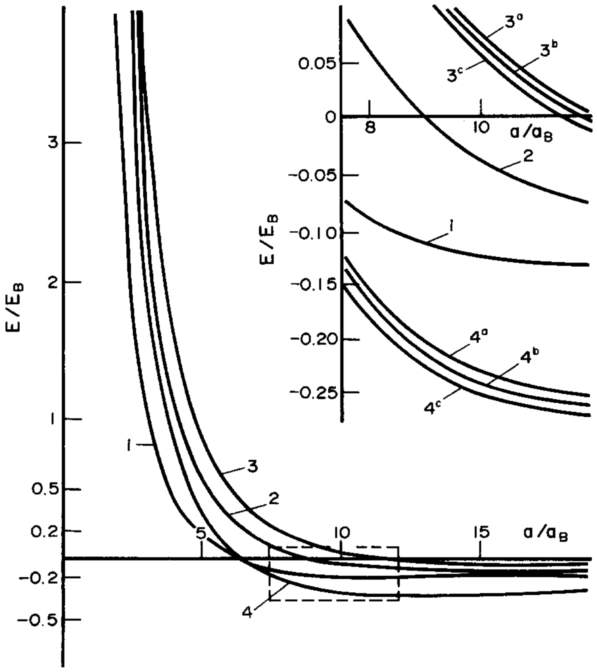

Fig.3 The bound energy dependencies of excitons, trions and biexcitons on microcrystal radius a. E_{ex}^- – 1, E_{ex}^+ –2; $E_{tr}(J)$ – 3a,3b,3c and $E_{bi}(J)$ – 4a,4b, 4c for J=0,1,2. The insert: the dependencies on a larger scale

state is the lowest hole state for all investigated a.

Confined trions and biexciton must be therefore formed in this case from the odd hole wave functions with F=1. Considering the hole spin one can show that there are only three two particle wave functions which satisfy the condition of the hole interchanging antisymmetry with total momentum J=0,1,2. The trion and biexciton energies have the following form in the case of strong size quantization:

$$E^{-}_{tr,bi}(J) = 2\,\frac{\hbar^2\varphi_1^2}{2m_h a^2} - A_{tr,bi}(J)\frac{e^2}{\kappa a} \quad (22)$$

where $A_{tr}(0)=1.660$, $A_{tr}(1)=1.760$, $A_{tr}(2)=1.705$, $A_{bi}(0)=3.112$, $A_{bi}(1) = 3.212$, $A_{bi}(2)=3.157$. The variationaly obtained E_{tr} and E_{bi} dependencies on a are shown in Fig.3. These dependencies over the range of all valuable a are well described by Eqs.19,22.

The overlap integrals (13,14) vanish in this approximation as far as the wave functions of odd hole states are formed only by the $Y_{1,m}$ with $l=1$. All considered exciton complexes are as a result optically nonactive in the case of small spin-orbit splitting Δ.

6. In conclusion, we have demonstrated the negative biexciton bound energy in small size microcrystals. It means that to create a second electron-hole pair it is necessary to have additional energy of exciting photons. This effect can to lead to the blue shift of absorption band edge at high intensity of excitation [15,8].

The other important result is the optical nonactivity of the exciton complexes and excitons in microcrystals with small Δ. It means that quantum efficiency has to decrease in small microcrystals when the hole quantum-size energy is larger then Δ. It might be an explanation of the absence of an interband luminescence in CdS microcristals of the small size [16].

REFERENCES

1. A.I.Ekimov, A.A.Onushchenco, Sov. Phys. Semicond. **16**, 775 (1982).
2. A.I.Ekimov, Al.L.Efros, A.A.Onushchenco, Solid State Commun. **56**, 921, (1985).
3. T.Iton, Y.Iwabuchi, M.Kataoka, Phys. Stat. Sol.**B** **145**, 567 (1988).
4. T.Iton, Y.Iwabuchi, T.Kirihara, Phys. Stat. Sol.**B** **146**, 531 (1988).
5. R.Rossetti, R.Hull, J.M.Gibson, L.E.Brus, J. Chem. Phys. **82**, 552, (1985).
6. N.Chestnoy, R.Hull, L.E.Brus, J. Chem. Phys. **85**, 2237 (1986).
7. L.E.Brus, J. Chem. Phys. **80**, 4403, (1984).
8. A.I.Ekimov, Al.L.Efros, Phys. Stat. Sol. **B** **150**, 627 (1988).
9. Al.L.Efros, A.L.Efros, Sov. Phys. Semicond. **5**, 1905 (1972).
10. Y.Kayanuma, Phys. Rev. B **38**, 9797 (1988).
11. J.M.Luttinger, Phys. Rev. **102**,1030 (1956).
12. B.L.Ge'lmont, M.I.D'yakonov, Sov. Phys. Semicond. 5, 1905 (1972).
13. B.L.Gel'mont, M.I.D'yakonov, Sov. Phys. Semicond. 7, 1345 (1974).
14. A.I.Akhiezer, V.B.Berestetskii, Quantum electrodinamics, Interscience, New York (1965).
15. U.V.Vandichev, V.S.Dneprovskii, A.I.Ekimov, D.K.Okorokov, L.B.Popova, Al.L.Efros, JETF Lett. **46**, 495 (1987).
16. A.I.Ekimov, I.A.Kudriavtsev, M.G. Ivanov, Al.L.Efros, Sov. Phys. Solid State **31**(8), 192 (1989).