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Exciton-Neutral-Donor Complexes in Semiconductor Quantum Dots

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The quantum states of exciton-neutral-donor complexes in semiconductor quantum dots are computed using a numerical matrix-diagonalization scheme. The results predict an increasing binding energy of exciton to neutral donor with decreasing dot size.

KEYWORDS: exciton-neutral-donor complex, quantum dot

1. Introduction

The size quantization of electronic states in semiconductor microcrystallites has been extensively investigated [1-9]. When the size of the crystallites is of the order of or less than the exciton Bohr radius, the quantum confinement effects lead to pronounced changes in their electronic and optical properties. The quantum confinement effects will also influence the interaction of electrons and holes with impurities in the quantum dots.

In this paper we present a theoretical calculation of the quantum states for exciton-neutral-donor complexes in quantum dots. In order to obtain reliable results of the binding energy of exciton to donor, both the exciton-neutral-donor complex state and the free exciton state must be calculated accurately. We do this using a matrix-diagnolization scheme.

2. Theoretical Formulation

The system of exciton-neutral-donor complex in a quantum dot is modeled as three particles, two electrons and one hole, moving in a spherical quantum well with a fixed charge located at the center of the sphere. The motion of the particles is described in effective mass approximation and the confinement is assumed to be an infinitive barrier. The Hamiltonian of the system is

$$H = -(\nabla_1^2 + \nabla_2^2) - \sigma\nabla_3^2 + \frac{2}{r_{12}} - \frac{2}{r_{13}} - \frac{2}{r_{23}} - \frac{2}{r_1} - \frac{2}{r_2} + \frac{2}{r_3} + U \ , \quad (1)$$

where $U = 0$ if all the particles are inside the sphere, and $U = +\infty$ otherwise. We have denoted the electron coordinates by the subscripts 1 and 2, and the hole coordinate by 3. $\sigma = m_e/m_h$ is the electron-to-hole effective-mass ratio. In eq (1), and throughout this paper, the unit of length is the donor Bohr radius $a_d = \varepsilon\hbar^2/m_e e^2$ and the unit of energy is the donor Rydberg $E_{dR} = m_e e^4/2\varepsilon^2\hbar^2$ with ε being the dielectric constant.

To compute the energies and eigenfunctions of Hamiltonian (1) we expand the eigenfunctions in a complete set of basis functions $\{|\overline{K}\rangle\}$. The basis functions are chosen as

$$|\overline{K}\rangle = A(1 + \hat{P}_{12})|K\rangle \ , \quad (2)$$

where

$$\begin{aligned} |K\rangle &\equiv |((n_1 l_1, n_2 l_2)L_{12}, n_3 l_3)LM\rangle \\ &= \sum_{m_3 M_{12}} \langle L_{12} M_{12} l_3 m_3 | LM\rangle \\ &\quad \times |\,(n_1 l_1, n_2 l_2)L_{12} M_{12}\rangle |n_3 l_3 m_3\rangle \ , \end{aligned} \quad (3)$$

$$|(n_1 l_1, n_2 l_2)L_{12} M_{12}\rangle = \sum_{m_1 m_2} \langle l_1 m_1 l_2 m_2 | L_{12} M_{12}\rangle \times |n_1 l_1 m_1\rangle |n_2 l_2 m_2\rangle \quad (4)$$

and $\hat{P}_{12}$ is the permutation operator on the electron 1 and electron 2; $A = 1/2$ if $n_1 = n_2$ and $l_1 = l_2$, and $A = \sqrt{2}/2$ otherwise. From the properties of the Clebsch-Gordan coefficient we have

$$\hat{P}_{12}|K\rangle = (-1)^{l_1+l_2-L_{12}}|((n_2 l_2, n_1 l_1)L_{12}, n_3 l_3)LM\rangle \quad (5)$$

The single-particle orbital functions $|nlm\rangle$ in eqs. (2)-(5) are defined by

$$\langle \mathbf{r}|nlm\rangle = R_{nl}(r)Y_{lm}(\theta,\varphi) \ , \quad (6)$$

where

$$R_{nl}(r) = \sqrt{\frac{2}{a^3}}\frac{j_l(z_{nl}r/a)}{j_{l-1}(z_{nl})} \ , \quad (7)$$

Y_{lm} is a spherical harmonic function, a is the radius of the sphere, z_{nl} is the nth zero of the l-degree spherical Bessel function $j_l(x)$. The total angular momentum is a constant of motion and therefore provides a good quantum number, L. In computing the states we can consider each L separately.

The matrix elements of the kinetic part of the Hamiltonian (1) on the base defined by eq. (2) can be obtained directly from

$$-\nabla_i^2|\overline{K}\rangle = (\frac{z_{n_i l_i}}{a})^2|\overline{K}\rangle, \quad i=1,2,3. \tag{8}$$

For the matrix elements of the Coulomb interactions we derive, using the tensor operator techniques, the following formulas

$$\langle K|r_{13}^{-1}|K'\rangle = \delta_{L,L'}\delta_{n_2n_2'}\delta_{l_2l_2'}(-1)^{L+l_2+k}$$
$$\times[L_{12},L_{12}',l_1,l_1',l_3,l_3']^{1/2}a^{-1}\sum_{k=0}^{\infty} I(n_1l_1n_1'l_1'n_3l_3n_3'l_3'k)$$
$$\times\begin{pmatrix} l_1\ k\ l_1' \\ 0\ 0\ 0\end{pmatrix}\begin{pmatrix} l_3\ k\ l_3' \\ 0\ 0\ 0\end{pmatrix}\begin{Bmatrix} L_{12}\ L_{12}'\ k \\ l_3'\ l_3\ L\end{Bmatrix}\begin{Bmatrix} L_{12}\ L_{12}'\ k \\ l_1'\ l_1\ l_2\end{Bmatrix}, \tag{9}$$

$$\langle K|r_{12}^{-1}|K'\rangle = \delta_{L,L'}\delta_{L_{12}L_{12}'}\delta_{n_3n_3'}\delta_{l_3l_3'}(-1)^{L_{12}+l_1-l_1'}$$
$$\times[l_1,l_1',l_2,l_2']^{1/2}a^{-1}\sum_{k=0}^{\infty} I(n_1l_1n_1'l_1'n_2l_2n_2'l_2'k)$$
$$\times\begin{pmatrix} l_1\ k\ l_1' \\ 0\ 0\ 0\end{pmatrix}\begin{pmatrix} l_2\ k\ l_2' \\ 0\ 0\ 0\end{pmatrix}\begin{Bmatrix} l_1'\ l_2'\ L_{12} \\ l_2\ l_1\ k\end{Bmatrix}, \tag{10}$$

$$\langle K|r_i^{-1}|K'\rangle = \Delta_i\frac{2}{a}\int_0^1 drP(n_i,l_i,r)P(n_i',l_i',r)r^{-1}$$
$$\text{for}\quad i=1,2,3 \tag{11}$$

where

$$I(n_1l_1n_1'l_1'n_2l_2n_2'l_2'k) = \int_0^1 drP(n_1,l_1,r)P(n_1',l_1',r)$$
$$\times\int_0^r dr'P(n_2,l_2,r')P(n_2',l_2',r')\frac{r'^k}{r^{k+1}}$$
$$-\int_0^1 drP(n_2,l_2,r)P(n_2',l_2',r)$$
$$\times\int_0^r dr'P(n_1,l_1,r')P(n_1',l_1',r')\frac{r'^k}{r^{k+1}}, \tag{12}$$

$$P(n,l,r) = \frac{\sqrt{2}\ r\ j_l(z_{nl}r)}{j_{l-1}(z_{nl})}, \tag{13}$$

$\begin{pmatrix} a\ b\ c \\ d\ e\ f\end{pmatrix}$ and $\begin{Bmatrix} a\ b\ c \\ d\ e\ f\end{Bmatrix}$ are the 3-j and 6-j symbols respectively. The Δ_i in eq. (11) is equal to one if $|K\rangle$ is identical to $|K'\rangle$ or different only in n_i and n_i'; otherwise $\Delta_i = 0$. We have also used the notations

$$[a,b,\cdots] = (2a+1)(2b+1)\cdots. \tag{14}$$

By virtue of eq. (5), all the Coulomb interaction matrix elements can be obtained from eqs. (9)-(14).

The binding energy of the exciton to neutral donor is defined by

$$B_{dx} = E_x + E_d - E_{dx} \tag{15}$$

where E_{dx} is the ground state energy of the confined exciton-neutral-donor complex, E_x and E_d are the ground state energies of the exciton and the donor separately confined in quantum dots. We compute E_x by diagonalizing the matrix of the exciton Hamiltonian[5]

$$H_x = -\nabla_e^2 - \sigma\nabla_h^2 - \frac{2}{|\mathbf{r}_e - \mathbf{r}_h|} + U \tag{16}$$

on the two particle basis functions,

$$|(n_el_e,n_hl_h)L_xM_x\rangle \tag{17}$$

The single-donor states are easily computed by diagonalizing the donor Hamiltonian

$$H_d = -\nabla^2 - \frac{2}{r} + U \tag{18}$$

on the single-particle basis functions, $|nlm\rangle$.

3. Numerical Results and Discussion

In order to obtain reliable exciton-neutral-donor binding energy, the exciton ground state energy E_x and the donor ground state energy E_d must be calculated accurately. In computing E_x we include 270 two-particle orbitals of the type specified by eq. (17) as basis functions for the exciton Hamiltonian H_x. The lowest eigenvalue E_x obtained from the diagonalization of the 270×270 H_x matrix is believed to be accurate enough when $a \leq 6a_x$, where a_x is the bulk exciton Bohr radius. In computing E_d we use 200 single-particle basis functions with $l=0$ for the H_d matrix, exceeding the accuracy requirement.

For exciton-neutral-donor complex states, the number of basis functions needed is much larger. We use 341 three-particle basis functions specified by eq. (1) for our explicit calculations. The angular integrals, products of 3-j and 6-j symbols, in eq. (9) and (10) are programmed efficiently. For the large number of radial integrals we make use of the symmetry properties

$$I(n_1l_1n_1'l_1'n_2l_2n_2'l_2'k) = I(n_2l_2n_2'l_2'n_1l_1n_1'l_1'k)$$
$$= I(n_1'l_1'n_1l_1n_2l_2n_2'l_2'k) \tag{19}$$

to simplify the numerical calculations.

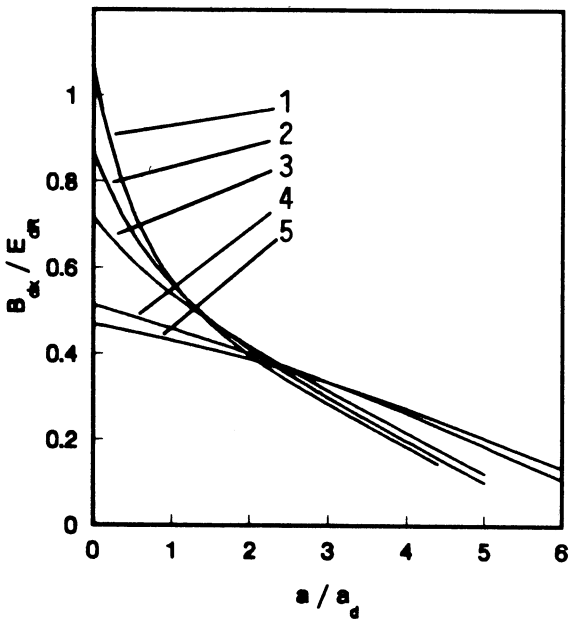

Fig.1. Exciton-neutral-donor binding energy B_{dx} as function of dot radius a for five different electron-hole mass ratios, m_e/m_h = 0.1 (curve 1), 0.15 (curve 2), 0.24 (curve 3), 0.69 (curve 4) and 1 (curve 5).

In practice, we evaluate the integrals I for all concerned combinations of $(n_1 l_1 n_1' l_1'' n_2 l_2 n_2' l_2'' k)$, store the results in a data file, and use that data file repeatedly in calculating the Coulomb interaction matrix. The total Hamiltonian matrix of the confined exciton-neutral-donor complex is then diagonalized to obtain energy E_{dx} and correspond eigenvectors.

The size dependence of the exciton-neutral-donor binding energy B_{dx} is calculated for a number of electron-hole mass ratios. Figure 1 shows the variations of the binding energy B_{dx} with the dot radius a for the mass ratios m_e/m_h = 1, 0.69, 0.24, 0.15 and 0.1. The parameters m_e/m_h =0.69, 0.24, 0.15 and 0.1 are chosen for ZnS, CdS, ZnTe and GaAs respectively.

From fig. 1 one can see that the exciton-neutral-donor binding energy is always positive and increases with the decrease of the dot size. When the radius of the sphere is about a_d the binding energy of exciton to neutral donor is an order of larger than that of in bulk sample[10]. For the physically unrealistic, but theoretically interasting limit $a \to 0$, we see that the exciton-to-neutral-donor energy approches values around the donor binding energy in the bulk.

References

1) A. I. Ekimov and A. A. Onushchenko, Sov. Phys. Semicond. **16** (1982) 775.
2) L. E. Brus, J. Chem. Phys. **80** (1984) 4403.
3) Y. Kayanuma, Solid State Commun. **59** (1986) 405.
4) T. Itoh and T. Kirihara, J. Lumin. **31/32**(1984)120.
5) Y. Chen and X. Xu, Chinese J. Lumin. **9** (1988) 85.
6) T. Takagahara, Phys. Rev. B **39** (1989) 10206.
7) S. Nomura and T. Kobayashi, Phys. Rev. B **45** (1991) 1305.
8) Y. Kayanuma, Phys. Rev. B **38** (1988) 9797.
9) Y. Wang, N. Herron, W. Mahler, and A. Sune, J. Opt. Sco. Am. **6** (1989) 808.
10) W. Ungier and M. Suffczynski, Phys. Rev. B **24** (1981) 2109.