

EXCITONIC ENERGY BANDS FORMATION IN QUANTUM DOT SUPERCRYSTALS

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Abstract

Nanocrystal solids with long range order is a new class of artificial materials, which physical properties are depend on the features of individual nanocrystals as well as their mutual interaction. In this work we investigate the energy band structure in a two-dimensional ordered array of semiconductor nanocrystals with degenerate valence band and finite value of spin-orbit splitting. The Coulomb interaction between nanocrystals splits energy of quantized states of individual nanocrystals into excitonic energy bands. By changing the geometry of lattice and material parameters of individual nanocrystal, one can control the electromagnetic properties of these artificial materials.

Keywords: Quantum dots, supercrystals, energy transfer

1. INTRODUCTION

Unlike atomic and molecular crystals whose lattice geometry and composition are immutable and determined by nature, nanocrystal solids, also known as quantum dot supercrystals allows to design their "crystalline" structure [1-3]. These artificial materials represent a new type of condensed matter systems with properties depend both on the individual features of building blocks and on many-body effects of their mutual interactions. To understand the properties of such systems is required to development of new theoretical approaches that would successfully combine methods of solid state physics as well as physics of mesoscopic systems.

In our previous work [4] we calculated energy spectra of excitonic bands in two-dimensional NC solids with different types of Bravais lattices. However, the simple model we used to describe an exciton structure in NCs does not take into account their materials parameters in calculations of Coulomb interactions. This paper aims to fill this gap. For this purpose we consider the interaction between NCs with degenerate valence band structure and finite value of spin-orbit splitting. We obtained the analytical expressions for matrix elements of Coulomb interaction between elementary interactions in semiconductor NCs. Using these expressions we calculate the excitonic energy bands corresponding to the simple two-dimensional lattices.

2. NONRADIATIVE EXCITON TRANSFER

Let us discuss the spherically symmetric NCs made of direct band gap, A_{III}B_{VI} or A_{III}B_{IV} semiconductors with cubic lattice structure. We assume that the radius of considered NCs is much smaller than the exciton Bohr radius in bulk material. That allows us to use strong confinement approximation and consider electron-hole mutual interaction perturbatively.

The confined states of electron are described by the following set of quantum numbers: $c = \{n_e, l_e, m_e, s_z\}$, where index n_e labels different states with the same symmetry in order of increasing energy, l_e is an electron orbital angular momentum, and m_e its projection, $s_z = \pm 1/2$ denotes spin projection. Each state are degenerate with respect to the spin projection as well as the projection of orbital angular momentum. The electron wave function in the envelope function approximation can be written as

$$\Psi_c(\mathbf{r}) = R_{n_e l_e}(r) Y_{l_e m_e}(\vartheta, \varphi) |S, s_z\rangle, \quad (1)$$

where $|S, s_z\rangle$ is the Bloch wave function at the bottom of s-type conduction band, $R_{n_e l_e}(r)$ and $Y_{l_e m_e}(\vartheta, \varphi)$ are radial and angular parts of the electron envelope function, respectively.

As opposed to electron states, the set of quantum numbers for confined hole states is $v = \{n_h, F, F_z, p\}$, where n_h labels the different states with the same symmetry in order of increasing energy, $F = 1/2, 3/2, \dots$ is an eigenvalue of total angular momentum, and F_z its projection, $p = \pm 1$ is parity of the state, since the holes Hamiltonian preserves the states symmetry with respect to inversion of coordinates. The total angular momentum F is the sum of valence band Bloch function angular momentum J and orbital angular momentum of the envelop function L : $F = L + J$. Each of these states are degenerate with respect to the projection of total angular momentum F_z . In the envelope function approximation the wave functions of hole states represent as the linear combination of the form

$$\Psi_v(\mathbf{r}) = \sum_{L,J} R_{n_h L J p}(r) \sum_{J_z=-J}^J C_{L, F_z - J_z; J, J_z}^{F F_z} Y_{L, F_z - J_z}(\vartheta, \varphi) |J, J_z\rangle, \quad (2)$$

where $|J, J_z\rangle$ is the valence band Bloch function at the top of p-type valence band, $C_{L, F_z - J_z; J, J_z}^{F F_z}$ is the Clebsch-Gordan coefficient. The radial parts $R_{n_h L J p}(r)$ with the different pairs (L, J) correspond to the branches of the bulk valence band: $(J = 3/2, L = F + p/2)$ for light-holes, $(J = 3/2, L = F - 3p/2)$ for heavy-holes, and $(J = 1/2, L = F + p/2)$ for split-off holes, respectively.

The interaction between neutral NCs which are located in different sites of NC solid lattice describes by the screened Coulomb potential,

$$V_{\mathbf{nm}} = \frac{e^2}{\varepsilon |\mathbf{r}_{\mathbf{nm}} + \mathbf{r}_{\mathbf{n}} - \mathbf{r}_{\mathbf{m}}|}, \quad (3)$$

where \mathbf{n} and \mathbf{m} are the position vectors of NCs, e is the elementary charge, $\mathbf{r}_{\mathbf{nm}}$ is the vector directed from the center of one NC to another, $\mathbf{r}_{\mathbf{n}}$ and $\mathbf{r}_{\mathbf{m}}$ are the radius-vectors of electrons in corresponding NCs, ε is the effective permittivity, which in general is a function $f(\varepsilon_{\mathbf{n}}, \varepsilon_{\mathbf{m}}, \varepsilon_M)$ of high-frequencies permittivity's of NCs $\varepsilon_{\mathbf{n}}$ and $\varepsilon_{\mathbf{m}}$, and environment ε_M [5]. This interaction results in excitation transfer from one NC to another. In the initial state there is an electron in the conduction band state c in NC located at \mathbf{n} and in the valence band state v in NC located at \mathbf{m} . In the final state there is an electron in conduction band state c' in \mathbf{m} and in valence band state v' in \mathbf{n} , respectively. The appropriate matrix element has the following form

$$M_{\mathbf{nm}} = \frac{e^2}{\varepsilon} \iint d\mathbf{r}_{\mathbf{n}} d\mathbf{r}_{\mathbf{m}} \frac{\Psi_{v'}^*(\mathbf{r}_{\mathbf{n}}) \Psi_{c'}^*(\mathbf{r}_{\mathbf{m}}) \Psi_c(\mathbf{r}_{\mathbf{n}}) \Psi_v(\mathbf{r}_{\mathbf{m}})}{|\mathbf{r}_{\mathbf{nm}} + \mathbf{r}_{\mathbf{n}} - \mathbf{r}_{\mathbf{m}}|}, \quad (4)$$

We assume that NCs are sufficiently separated and there is no overlap between their wave functions. Thus, we do not include the exchange interaction term in Eq. (4).

In order to separate the variables relating to the different NCs in Eq. (4), we use the following Fourier integral representation:

$$\frac{1}{|\mathbf{r}_{\mathbf{nm}} + \mathbf{r}_{\mathbf{n}} - \mathbf{r}_{\mathbf{m}}|} = \frac{1}{2\pi^2} \int \frac{d\mathbf{q}}{q^2} e^{i\mathbf{q}(\mathbf{r}_{\mathbf{nm}} + \mathbf{r}_{\mathbf{n}} - \mathbf{r}_{\mathbf{m}})} \quad (5)$$

then

$$M_{\mathbf{nm}} = \frac{1}{2\pi^2} \frac{e^2}{\varepsilon} \int \frac{d\mathbf{q}}{q^2} \mathcal{F}_{c'v'}^{(\mathbf{n})}(\mathbf{q}) \mathcal{F}_{cv}^{(\mathbf{m})*}(\mathbf{q}) e^{i\mathbf{q}\mathbf{r}_{\mathbf{nm}}}, \quad (6)$$

where

$$\mathcal{F}_{cv}^{(\mathbf{a})}(\mathbf{q}) = \int d\mathbf{r}_{\mathbf{a}} \Psi_c(\mathbf{r}_{\mathbf{a}}) \Psi_v(\mathbf{r}_{\mathbf{a}}) e^{i\mathbf{q}\mathbf{r}_{\mathbf{a}}}. \quad (7)$$

The envelope function approximation allows us to separate the integration of Bloch and envelope functions in Eq. (7), then we obtain

$$\mathcal{F}_{cv}^{(\mathbf{a})}(\mathbf{q}) = i \sum_{L, J, J_z} (\mathbf{q} \cdot \boldsymbol{\rho}_{JJ_z S_z}^{(\mathbf{a})}) \sigma_{LJJ_z}^{(\mathbf{a})}(\mathbf{q}) \quad (8)$$

where $\rho_{JJ_z S_z}^{(a)} = \langle JJ_z | \mathbf{r}_a | S_z \rangle$ is the bulk interband matrix element of the radius-vector, and

$$\sigma_{LJJ_z}^{(a)}(\mathbf{q}) = \int d\mathbf{r}_a e^{i\mathbf{q}\mathbf{r}_a} \psi_c(\mathbf{r}_a) \psi_v(\mathbf{r}_a), \quad (9)$$

$\psi_c(\mathbf{r}_a)$ and $\psi_v(\mathbf{r}_a)$ are the envelope functions of electron and states, respectively. Since the confinement potential of considering NCs has the spherical symmetry it is convenient to use the representation of plane waves by the spherical harmonics. After evaluating the angular part Eq. (9) depends only on absolute value of q and has the following form

$$\sigma_{LJJ_z}^{(a)}(q) = C_{L,F_z-J_z;J,J_z}^{FF_z} \sqrt{\frac{2L+1}{2l_e+1}} \sum_{k=0}^{\infty} \Omega_k J_k^{(a)}(q) \quad (10)$$

where

$$\Omega_k = (i)^k (2k+1) C_{l_e 0; k 0}^{L 0} C_{l_e m_e; k 0}^{L, F_z - J_z} \quad (11)$$

and

$$J_k^{(a)}(q) = \int_0^{R_a} dr_a R_{n_e l_e}(r_a) R_{n_h L J_p}(r_a) j_k(qr_a), \quad (12)$$

R_a is the nanocrystal radius, $j_k(x)$ is the spherical Bessel function. The Clebsch-Gordan coefficients in Eq. (11) determine the selection rules for multipole interband transitions due to the energy transfer: $|l_e - k| \leq L \leq l_e + k$, $L + l_e + k = \text{even number}$ and $m_e = F_z - J_z$. Therefore, a nonzero contribution to Eq. (8) provides by terms with $J_z = F_z - m_e$.

Returning to the Eq. (6) carry out the integration over angular variables, choosing z axis whose direction coincides with vector \mathbf{r}_{nm} . Eventually we obtain the following expression:

$$M_{nm} = \frac{e^2}{\varepsilon \mathbf{r}_{nm}^3} \sum_{LL', JJ'} \left[\left(\rho_{J'J'_z S'_z}^{(n)} \cdot \rho_{JJ_z S_z}^{(m)} \right) I_{LL', JJ'}^{(1)} - 3 \left(\mathbf{e}_{nm} \cdot \rho_{JJ_z S_z}^{(m)} \right) \left(\mathbf{e}_{nm} \cdot \rho_{J'J'_z S'_z}^{(n)} \right) I_{LL', JJ'}^{(2)} \right] \quad (13)$$

$$I_{LL', JJ'}^{(t)} = \left(\frac{1}{3} \right)^{t-1} \frac{2}{\pi} \int_0^{\infty} dx x^t j_t(x) \sigma_{L'J'J'_z}^{(n)}(x/\mathbf{r}_{nm}) \sigma_{LJJ_z}^{(m)*}(x/\mathbf{r}_{nm}), \quad (14)$$

where \mathbf{e}_{nm} is the unit vector co-directional with \mathbf{r}_{nm} . At first sight expression (13) is similar to well-known matrix element of dipole-dipole interactions in atomic and molecular systems [6], except coefficients $I_{LL', JJ'}^{(t)}$ that include contribution of high-multipole interactions as well as nanocrystals material parameters.

In the dipole-dipole approximation ($L' = l_e$ and $L = l'_e$) the matrix element (13) is given by

$$M_{nm} = \frac{e^2}{\varepsilon \mathbf{r}_{nm}^3} \sum_{LL', JJ'} K_{L'J'}^{(n)} K_{LJ}^{(m)*} \left[\left(\rho_{J'J'_z S'_z}^{(n)} \cdot \rho_{JJ_z S_z}^{(m)} \right) - 3 \left(\mathbf{e}_{nm} \cdot \rho_{JJ_z S_z}^{(m)} \right) \left(\mathbf{e}_{nm} \cdot \rho_{J'J'_z S'_z}^{(n)} \right) \right], \quad (15)$$

where

$$K_{LJ}^{(a)} = C_{L, F_z - J_z; J, J_z}^{FF_z} \int_0^{R_a} dr_a r_a^2 R_{n_e l_e}(r_a) R_{n_h L J_p}(r_a), \quad (16)$$

In contrast to calculations in two-band approximation [7], Eq. (15) allowed transitions between states with different quantum numbers n_e and n_h , and also contains envelope functions overlap integrals (16). It should be noted that in this case the effective permittivity ε is given by [5, 7]

$$\varepsilon = \frac{(\varepsilon_{NC} + 2\varepsilon_M)^2}{9\varepsilon_M} \quad (17)$$

where ε_{NC} is the NCs high-frequency permittivity. In our further calculations we assume that NCs are embedded in a wide-gap dielectric matrix, so that we use the infinite walls approximation for quantum

confinement potential. Thus, the exact forms of the radial part functions and eigenenergy equation for carriers in NCs are chosen in accordance with Ekimov, et al. [8].

3. ENGINEERING EXCITONIC BANDS

To demonstrate the possibility of formation excitonic bands let us assume that NC solids forming simple two-dimensional rectangular lattice. The position of each NC may be denoted by vector $\mathbf{n} = n_1\mathbf{a} + n_2\mathbf{b}$, where \mathbf{a} and \mathbf{b} are the lattice translation vectors, n_1 and n_2 are integers. In this work in accordance with Heitler-London approximation we consider only lowest-energy excited states in NCs, and do not take into account the impact of high-energy excited states on exciton energy spectrum, therefore the interaction between NCs excitations could be described by dipole-dipole mechanism (15). This assumption is valid since the dephasing rate of such states is minimal, contributing to the formation of exciton coherent states in NC solids. If the excited state is f -fold degenerate it corresponds to f or less excitonic energy bands in supercrystal. In organic solids such partial or total degeneracy removal is called the Bethe splitting [9]. This effect caused to intermolecular interaction and translation symmetry of the crystal, which is lower than in a single molecule.

In the Heitler-London approximation the energy spectrum of excitons can be found through the diagonalization of the resonant interaction matrix L , which elements are given by [9]

$$L_{\alpha\beta}(\mathbf{k}) = \sum_{\mathbf{n} \neq \mathbf{m}} M_{\mathbf{nm}}^{\alpha\beta} \exp[i\mathbf{k}(\mathbf{n} - \mathbf{m})] \quad (18)$$

where α and β denote the degenerate energy states with different sets of quantum numbers, \mathbf{k} is the exciton wave vector, \mathbf{n} and \mathbf{m} are lattice translation vectors, and the matrix element $M_{\mathbf{nm}}^{\alpha\beta}$ is given by Eq. (13) in the general case. It should be note here that for calculation of matrix elements we need to express the electron's radius-vector $\mathbf{r}'(x', y', z')$ of each NC in the system associated with NC solid lattice through the radius vector $\mathbf{r}(x, y, z)$ of the same electron in the crystallographic system. Such coordinate transformations can be performed by using rotation matrix \mathcal{R} whose elements can be defined in different ways, for example, through the Euler angles. However, if crystallographic axes of all NCs are oriented identically, the energies of excitonic bands do not depend on the elements of rotation matrix \mathcal{R} [4]. As a rule the lowest-energy exciton state in colloidal semiconductor NCs is $1S_e - 1S_{3/2}$ which is eight-fold degenerate excluding electron-hole interactions. The energy of excitonic bands has the following form

$$E_\gamma(\mathbf{k}) = E_{ex} + D\mathcal{E}_\gamma(\mathbf{k}) \quad (19)$$

where

$$D = \frac{e^2}{\epsilon a^3} \left(\frac{P}{E_g} \right)^2 |K_{0,3/2}|^2 \quad (20)$$

is the coefficient measured in energy units and depending only on material parameters of NCs, and $\mathcal{E}_\gamma(\mathbf{k})$ is the γ th eigenvalue of the resonance interaction matrix (18), which depends only on geometry of supercrystal lattice, P is the Kane matrix element, and E_g is the NCs band gap.

Since the bulk interband matrix elements $\rho_{JJ_z S' z}^{(\alpha)}$ for the transitions $|3/2, 3/2\rangle \rightarrow |S, -1/2\rangle$ and $|3/2, -3/2\rangle \rightarrow |S, 1/2\rangle$ are zeroes, the resonance interaction matrix reduces to 6×6 matrix. Furthermore, the operator of NCs interaction (3) does not include the components that affect on electrons and holes spins, thus, the matrix elements (13) for the states with equal absolute values of exciton full angular momentum projections are indistinguishable. Therefore, there are only three excitonic bands correspond to the unique nonzero eigenvalues of hermitian matrix (18). Since the value of interaction matrix element (13) decreases with increasing distance as the $|r_{\mathbf{nm}}|^{-3}$, we can retain in (18) only terms correspond to the interaction with the nearest neighbors. Finally, the expressions of excitonic bands energy for the rectangular two-dimensional lattice are given by

$$\begin{aligned}
 \varepsilon_1(\mathbf{k}) &= \frac{8}{3} \left[\cos(k_x a) + \frac{1}{\delta} \cos(k_y a) \right] \\
 \varepsilon_2(\mathbf{k}) &= \frac{8}{3} \left[\cos(k_x a) - \frac{2}{\delta} \cos(k_y a) \right] \\
 \varepsilon_3(\mathbf{k}) &= -\frac{8}{3} \left[2\cos(k_x a) - \frac{1}{\delta} \cos(k_y a) \right]
 \end{aligned} \tag{21}$$

where $\delta = b/a$.

4. CONCLUSION

We theoretically investigate the Coulomb interaction between NCs with degenerate valence band and obtained the analytical expressions for matrix elements of energy transfer between them. We demonstrate that arrangement of semiconductor NCs in two-dimensional lattices results in formation of three excitonic energy bands, which properties are depend on material parameters of individual NCs and geometry of lattices. This possibility of tuning the properties of such artificial materials makes them interesting to using as building blocks in new devices for optoelectronics and photonics.

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