A THEORY OF LOW-TEMPERATURE STATIONARY PHOTOLUMINESCENCE OF A QUANTUM-DOT MOLECULE

Vadim K. Turkov[a], Stanislav Yu. Kruchinin[b], Ivan D. Rukhlenko [a,c], Anvar S. Baimuratov [a], Mikhail Yu. Leonov[a] , Yurii K. Gun'ko[a,d], Alexander V. Baranov [a] , Anatoly V. Fedorov[a]

[a] *ITMO University, 49 Kronverkskiy pr., Saint-Petersburg, 197101, Russia; vadim.turkov@gmail.com*

[b] *Max Plank Institute of Quantum Optics, Hans-Kopfermann-Straße 1, D-85748 Garching, Germany*

[c] *Monash University, Clayton Campus, Victoria 3800, Australia*

[d] *School of Chemistry and CRANN Institute, Trinity College, Dublin, Dublin 2, Ireland*

Abstract

We have developed a theory of low-temperature, stationary photoluminescence from a pair of spherical quantum dots coupled by the Coulomb interaction in a quantum-dot molecule. The interdot Coulomb interaction can lead to both the incoherent and coherent energy transfers in the closely packed assemblies of quantum dots, just as it does in atomic and molecular systems. In this work we present a theory on the secondary emission from a pair of coherently coupled quantum dots and analyzing the manifestations of coherence effects in the photoluminescence spectra The lowest-energy electron-hole-pair states of the dots were assumed to be nearly resonant and characterized by low decay and dephasing rates. The coherent coupling of the quantum dots under these conditions was shown to manifest itself in the molecule's photoluminescence spectrum as a pair of peaks, the intensities and spectral positions of which are determined by the geometry (quantum dot sizes and distance between them) and material of the nanocrystals, as well as by the rates of the energy and phase relaxations of their electronic subsystems. We also derived an expression for the photoluminescence differential cross section, which is useful for interpreting and analyzing the secondary emission spectra of coherently coupled quantum dots.

Keywords:

Quantum dots, secondary emission, energy transfer

1. INTRODUCTION

Nonradiative electronic energy transfer in quantum dots (QDs) has received much attention in the recent theoretical and experimantal studies due to its promising applications in biology and medicine [1], artificial light-harvesting assemblies and optoelectronic devices [2], and quantum computing [3]. This problem becomes essential for optical and transport properties of close-packed quantum dot structures, such as QDs supercrystals [4]. Quantum dot ensembles also present a good model system for investigation of resonant energy transfer phenomenon by methods of optical spectroscopy, due to the size-dependent energy spectrum, chemical stability and brightness of QDs. Moreover, theoretical description of energy transfer in certain types of nanocrystals can be performed in the framework of simple dipole-dipole approximation even at quasicontact distances [5-6].

In our previuos works [7-9] we studied the stationary photoluminescence of semiconductor quantum dots with consideration for incoherent irreversible and reversible regimes of resonant energy transfer. Thus, there is a problem to develop the theoretical description of secondary emission from coherently coupled quantum dots and to find the manifestations of the coherent effects in the photoluminescence spectra.

In this work we presenting a theoretical analysis of the secondary emission from a pair of coherently coupled QDs - quantum-dot molecule (QDM).

2. QUANTUM-DOT MOLECULE IN ELECTROMAGNETIC FIELD

Electrons confined in two QDs interacting with the classical optical field and the quantum electromagnetic field of the vacuum can be generally described by the Hamiltonian

$$H = H_{QDM} + H_R + H_{QDM,L} + H_{QDM,R}, \tag{1}$$

where the first term describes the noninteracting QDM, second term represents emmited photons. The last two terms represent the interactions between laser field (L) and vacuum of electromagnetic radiation (R), respectively.
Let us consider the QDM Hamiltonian

$$H_{QDM} = \sum_{\alpha}\sum_{p} E_{p,\alpha} a^{+}_{p,\alpha} a_{p,\alpha} + \sum_{p,q}\left(M_{q\mathrm{I},p\mathrm{II}} a^{+}_{q,\mathrm{I}} a_{p,\mathrm{II}} + \mathrm{H.c.}\right), \tag{2}$$

where $E_{p,\alpha}$ is the energy of the electron-hole pair state p for first ($\alpha = \mathrm{I}$) or second ($\alpha = \mathrm{II}$) QD, $a^{+}_{p,\alpha}$ and $a_{p,\alpha}$ are the creation and annihilation operators of the electron-hole pairs, respectively. The matrix element $M_{q\mathrm{I},p\mathrm{II}} = \langle q,\mathrm{I}|V_C|q,\mathrm{II}\rangle$ represents the interdot interaction of electron-hole pairs coupled through the screened Coulomb potential

$$V_C(\mathbf{r},\mathbf{r}_{\mathrm{I}},\mathbf{r}_{\mathrm{II}}) = \frac{e^2}{\varepsilon|\mathbf{r}+\mathbf{r}_{\mathrm{I}}-\mathbf{r}_{\mathrm{II}}|}, \tag{3}$$

where $|p,\alpha\rangle$ is the electron-hole pair state, $\mathbf{r}_{\mathrm{I}}$ and $\mathbf{r}_{\mathrm{II}}$ are the radius vectors of electrons, originating from the center of the corresponding quantum dot, $\mathbf{r}$ is the vector directed from the center of the second to the center of the first quantum dot (hereafter we assume that QDs have a spherical shape) and ε is the effective dielectric constant [5, 8]

$$\varepsilon = \frac{(\varepsilon_{\mathrm{I}} + 2\varepsilon_M)(\varepsilon_{\mathrm{II}} + 2\varepsilon_M)}{9\varepsilon_M}, \tag{4}$$

$\varepsilon_{\mathrm{I}}, \varepsilon_{\mathrm{II}}, \varepsilon_M$ are the high-frequency dielectric constants of the QDs and matrix, respectively.

The Hamiltonian of noninteracting photons has the form

$$H_R = \sum_k \hbar\omega_k b^{+}_k b_k, \tag{5}$$

where b^{+}_k and b_k are the operators of the creation and annihilation of photons of the k-mode with frequency ω_k.

$$H_{QDM,L} = \sum_{\alpha}\sum_{p,k} g_{\alpha k}\left(i\hbar V^{(k)}_{p\alpha,0\alpha} b_k a^{+}_{p,\alpha} + \mathrm{H.c.}\right), \tag{6}$$

$$H_{QDM,R} = \sum_{\alpha}\sum_{p}\left(\varphi(t)V^{(L)}_{p\alpha,0\alpha}e^{-i\omega_L t}a^{+}_{p\alpha} + \text{H.c.}\right), \tag{7}$$

where $g_{\alpha k} = \sqrt{2\pi\omega_k / \varepsilon_\alpha \hbar V}$, ε_α is the dielectric constant of the corresponding QD, V is the normalization volume, $V^{(\eta)}_{p\alpha,0\alpha} = \langle p,\alpha|(-e\mathbf{r})\mathbf{e}_\eta|0,\alpha\rangle\,(\eta = L,k),(-e\mathbf{r})$ is the dipole momentum operator, $\mathbf{e}_\eta$ is the polarization vector, and $\varphi(t)$ is the complex envelope of the excitation field of frequency ω_L.

The most advantageous condition for realization of coherent coupling occurs when the resonance takes place between the lowest excited electronic states of quantum dots. This implies the following expression for Hamiltonian of QDM:

$$H_{QDM} = E_{\mathrm{I}}a^{+}_{\mathrm{I}}a_{\mathrm{I}} + E_{\mathrm{II}}a^{+}_{\mathrm{II}}a_{\mathrm{II}} + \langle 0,1|V_C|1,0\rangle a^{+}_{\mathrm{II}}a_{\mathrm{I}} + \langle 1,0|V_C|0,1\rangle a^{+}_{\mathrm{I}}a_{\mathrm{II}}, \tag{8}$$

where E_{I} and E_{II} are the energies of the lowest excited states of the electron-hole pairs. Hereafter we use the following notation for the wavefunctions of noninteracting QDs $|00\rangle = |0,\mathrm{I}\rangle|0,\mathrm{II}\rangle$, $|10\rangle = |1,\mathrm{I}\rangle|0,\mathrm{II}\rangle$, $|01\rangle = |0,\mathrm{I}\rangle|1,\mathrm{II}\rangle$. Note, that we neglect the interdot exchange interaction due to its weakness in the quantum dots grown in dielectric matrices [10].

We assume that QDs have a spherical shape and coupled through the screened Coulomb interaction. To describe the electronic states of quantum dots we use the approximation of infinitely high potential walls, two-band model, and assume that the the charge carriers are strongly confined. Since the interband transitions in both QDs are dipole-allowed, the matrix element of the Coulomb potential calculated in dipole-dipole approximation is given by [8]

$$M_{\mathrm{I,II}} = \langle 10|V_C|01\rangle = \frac{e^2\chi}{\varepsilon r^3}\left|\mathbf{r}^{(\mathrm{I})}_{vc}\right|\left|\mathbf{r}^{(\mathrm{II})}_{cv}\right|, \tag{9}$$

where $\left|\mathbf{r}^{(\alpha)}_{vc}\right| = P_\alpha / E^{(\alpha)}_g$ is the matrix element of the coordinate operator, P_α is the Kane parameter and $E^{(\alpha)}_g$ is the bandgap of the QDs semiconductor. Orientation dependence of matrix element is determined by the following function [11]

$$\chi(\theta_{\mathrm{I}},\theta_{\mathrm{II}},\phi) = \sin\theta_{\mathrm{I}}\sin\theta_{\mathrm{II}}\cos\phi - 2\cos\theta_{\mathrm{I}}\cos\theta_{\mathrm{II}}. \tag{10}$$

Vectors $\mathbf{r}_{\mathrm{I}}$ and $\mathbf{r}_{\mathrm{II}}$ make angles θ_{I} and θ_{II} with $\mathbf{r}$, and ϕ is the difference between their azimuth angles.

In order to develop a correct description of the photoluminescence from coherently coupled quantum dots, it is necessary choose the initial approximation of perturbation theory as a superposition of donor and acceptor states. This can be performed by the introduction of the following operators

$$\begin{pmatrix} a^{+}_1 \\ a^{+}_2 \end{pmatrix} = S_\upsilon \begin{pmatrix} a^{+}_{\mathrm{I}} \\ a^{+}_{\mathrm{II}} \end{pmatrix},\ S_\upsilon = \begin{pmatrix} \cos\upsilon & \sin\upsilon \\ -\sin\upsilon & \cos\upsilon \end{pmatrix}, \tag{11}$$

where $\upsilon = (1/2)\arctan\left(2M_{\mathrm{I,II}}/(E_{\mathrm{I}} - E_{\mathrm{II}})\right)$ $(-\pi/4 < \upsilon < \pi/4)$ is the angle of transformation which is similar to the parameter obtained in perturbation theory for degenerated states. In other words, correct basis functions $|1\rangle\rangle$, $|2\rangle\rangle$ and their respective eigenvalues $E_{1,2}$ should be defined as follows

$$\begin{aligned}\left|1\right\rangle\!\right\rangle &= \left|10\right\rangle\cos\upsilon + \left|01\right\rangle\sin\upsilon,\\ \left|2\right\rangle\!\right\rangle &= \left|01\right\rangle\cos\upsilon - \left|10\right\rangle\sin\upsilon,\end{aligned} \tag{12}$$

$$E_{1,2} = \frac{1}{2}\left(E_{\mathrm{I}} + E_{\mathrm{II}}\right) \pm \frac{1}{2}\sqrt{\left(E_{\mathrm{I}} - E_{\mathrm{II}}\right)^2 + 4\left|M_{\mathrm{I,II}}\right|^2}\,. \tag{13}$$

The Hamiltonian of interaction between coupled quantum dots and the single-mode classical optical field with frequency ω_L is given by the following expressions

$$\begin{aligned}H_{QDM,L} &= H_{1,L} + H_{2,L}\\ H_{\beta,L} &= \varphi(t)e^{-i\omega_L t}V_{1,0}^{(\beta L)}a_\beta^+ + \mathrm{H.c.},\ \beta = 1,2\end{aligned} \tag{14}$$

where

$$\begin{pmatrix}V_{1,0}^{(1L)}\\ V_{1,0}^{(2L)}\end{pmatrix} = S_\upsilon\begin{pmatrix}V_{1\mathrm{I},0\mathrm{I}}^{(L)}\\ V_{1\mathrm{II},0\mathrm{II}}^{(L)}\end{pmatrix}, \tag{15}$$

The operator describing the interaction of QDs with the quantum electromagnetic field can be written as

$$\begin{aligned}H_{QDM,R} &= H_{1,R} + H_{2,R}\\ H_{\beta,R} &= iB_\beta a_\beta^+ - iB_\beta^+ a_\beta,\ \beta = 1,2\end{aligned}, \tag{16}$$

where

$$\begin{pmatrix}B_1\\ B_2\end{pmatrix} = S_\upsilon\begin{pmatrix}g_{\mathrm{I},1R}V_{1\mathrm{I},0\mathrm{I}}^{(1R)}b_{1R}\\ g_{\mathrm{II},2R}V_{1\mathrm{II},0\mathrm{II}}^{(2R)}b_{2R}\end{pmatrix}, \tag{17}$$

3. PHOTOLUMINESCENCE OF A QUANTUM-DOT MOLECULE

We consider reduced two-point density matrix that describes the secondary emission from quantum dots in the following basis:

$$\left|1\right) = \left|00\right\rangle\!\left|0R\right\rangle,\ \left|2\right) = \left|1\right\rangle\!\right\rangle\left|0R\right\rangle,\ \left|3\right) = \left|2\right\rangle\!\right\rangle\left|0R\right\rangle,\ \left|4\right) = \left|00\right\rangle\!\left|1R\right\rangle,\ \left|5\right) = \left|00\right\rangle\!\left|2R\right\rangle \tag{18}$$

where $\left|1R\right\rangle$ and $\left|2R\right\rangle$ are the states of emitted photons.

Dynamics of this system is described by the generalized master equation for the reduced density matrix [12]

$$\frac{d}{dt}\rho_{ij} = \frac{1}{i\hbar}\left[H,\rho\right]_{ij} + \delta_{ij}\sum_{k\neq j}\zeta_{jk}\rho_{kk} - \gamma_{ij}\rho_{ij}, \tag{19}$$

where γ_{ii} is the population relaxation rate of the state i inversely proportional to its lifetime, $\gamma_{ij} = (\gamma_{ii} + \gamma_{jj})/2 + \hat{\gamma}_{ij}$ for $i \neq j$ is the dephasing rate of transition $|j\rangle \to |i\rangle$, $\hat{\gamma}_{ij}$ is the pure dephasing rate of the corresponding transition, ζ_{ij} is the rate of transition $|j\rangle\rangle \to |i\rangle\rangle$ due to interaction with the bath.

Considering a stationary laser excitation $\varphi(t) = E_L = const$ and performing a calculation in the lowest order of perturbation theory by interaction with electromagnetic fields, one can obtain the luminescence differential cross section (LDCS) per unit solid angle $d\Omega$ and per unit of frequency ω_k. Differential cross-sections are connected with photon emission rates W_1 and W_2 by the following relation

$$\frac{d\sigma_i}{d\Omega d\omega_{iR}} = \frac{V\hbar\omega_{iR}^3}{4(\pi c)^3}\frac{W_i}{I_L}, \tag{20}$$

where I_L is the excitation light intensity. With this relationship, the major contributions to the LDCS from the excited states of the QDM are found to be

$$\frac{d\sigma_1}{d\Omega d\omega_{1R}} \approx C(\omega_{1R})\left|V_{1\mathrm{I},0\mathrm{I}}^{(1R)}\right|^2\left[\cos^2\upsilon\left|V_{1,0}^{(1L)}\right|^2\frac{2}{\gamma_{11}}\frac{\gamma_{01}}{\gamma_{01}^2+\Delta_{1,1R}^2}\frac{\gamma_{01}}{\gamma_{01}^2+\Delta_{1,L}^2}\right.$$
$$\left.+\sin^2\upsilon\frac{\gamma_{02}}{\gamma_{02}^2+\Delta_{2,1R}^2}\frac{2}{\gamma_{22}}\left(\left|V_{1,0}^{(2L)}\right|^2\frac{\gamma_{02}}{\gamma_{02}^2+\Delta_{2,L}^2}+\left|V_{1,0}^{(1L)}\right|^2\frac{\zeta_{21}}{\gamma_{11}}\frac{\gamma_{01}}{\gamma_{01}^2+\Delta_{1,L}^2}\right)\right], \tag{21}$$

and

$$\frac{d\sigma_2}{d\Omega d\omega_{2R}} \approx C(\omega_{2R})\left|V_{1\mathrm{II},0\mathrm{II}}^{(2R)}\right|^2\left[\sin^2\upsilon\left|V_{1,0}^{(1L)}\right|^2\frac{2}{\gamma_{11}}\frac{\gamma_{01}}{\gamma_{01}^2+\Delta_{1,2R}^2}\frac{\gamma_{01}}{\gamma_{01}^2+\Delta_{1,L}^2}\right.$$
$$\left.+\cos^2\upsilon\frac{\gamma_{02}}{\gamma_{02}^2+\Delta_{2,2R}^2}\frac{2}{\gamma_{22}}\left(\left|V_{1,0}^{(2L)}\right|^2\frac{\gamma_{02}}{\gamma_{02}^2+\Delta_{2,L}^2}+\left|V_{1,0}^{(1L)}\right|^2\frac{\zeta_{21}}{\gamma_{11}}\frac{\gamma_{01}}{\gamma_{01}^2+\Delta_{1,L}^2}\right)\right]. \tag{22}$$

4. CONCLUSION

We have developed a theoretical description of the stationary photoluminescence from symmetric quantum dot molecule. Our results concerns coherent regime of resonant energy transport that occurs when the energy transfer rate overcomes the phase relaxation rate. Analytical expressions for the luminescence differential cross-section have been obtained.

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