Resonant electronic excitation energy transfer by
Dexter mechanism in the quantum dot system

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Abstract. In present work the energy transfer between quantum dots by the exchange
(Dexter) mechanism is analysed. The interdot Coulomb interaction is taken into consideration.
It is assumed that the quantum dot-donor and the quantum dot-acceptor are made from the
same compound A\textsubscript{3}B\textsubscript{5} and embedded in the matrix of other material creating potential barriers
for electron and holes. The dependences of the energy transfer rate on the quantum-dot system
parameters are found using the Kane model that provides the most adequate description spectra
of semiconductors A\textsubscript{3}B\textsubscript{5}. Numerical calculations show that the rate of the energy transfer by
Dexter mechanism is comparable to the rate of the energy transfer by electrostatic mechanism
at the distances approaching to the contact ones.

1. Introduction

Methods based on nonradiative energy transfer between quantum dots are in considerable current
use in biology and medicine. The strong dependence of the energy transfer rate on the distance
between the energy donor and the energy acceptor enables to detect the formation of antigen-
antibody complexes, enzyme-substrate complexes, the DNA hybridization and cleavage [1]
and also to study the structure and dynamics of biomolecules, where measurements of small
distance within the molecule are necessary [2–4]. Results of these investigations are of the great
importance for diagnostics and therapy of diseases, among which are oncological ones [5], (see
also the literature in [1]). A correct interpretation of experimental data requires the adequate
theory development. Resonant electronic excitation energy transfer occurs due to electric-
dipole-dipole, electric-dipole-quadrupole and higher multipole interactions and the exchange
interactions between the energy donor and the energy acceptor. The first interactions are of
an electrostatic nature, the last one has its origin in the antisymmetry of the electronic wave
function of the system including an energy donor and an energy acceptor. An equality of electron
excitation energies in donor and acceptor is a necessary condition for the resonant energy transfer
which follows from the energy conservation law. The theory descriptive of the energy transfer
between molecules due dipole-dipole interaction has been developed by Forster [6]. Subsequently,
Dexter developed the theory to describe the electrostatic and exchange mechanisms of the energy
transfer between impurity atoms or ions in an insulating crystal [7]. It was indicated that the
exchange contribution in the energy transfer can be important in two situations: first, distance
between donor and acceptor is short and the donor and acceptor wave functions are not strong
localized; second, a dipole-dipole transitions in the acceptor are forbidden. The use of the semiconductor quantum dots as the energy donor and the energy acceptor allows room for a wider range of biological and medicine experiments [8]. Theoretical description for the energy transfer between quantum dots by electrostatic mechanism was elaborated in [9, 10] assuming that the interactions between the quantum dot-donor electron and the quantum dot-acceptor electron is described by a Coulomb potential including all multipole terms. In present work the energy transfer between two quantum dots by the exchange mechanism is analyzed. The interdot Coulomb interaction is taken into consideration. It is assumed that the quantum dot-donor and the quantum dot-acceptor are made from the same compound A3B5 and placed in a matrix from other material creating potential barriers of finite heights for electrons (\(V_{cD}, V_{cA}\)) and holes (\(V_{hD}, V_{hA}\)). The quantum dots are separated by a finite distance \(d\). The system of two quantum dots is represented schematically in fig. 1. The energy transfer process is sketched in fig. 2.

**Figure 1.** Diagram of two quantum dots: a donor of radius \(R_D\) and an acceptor of radius \(R_A\).

**Figure 2.** Schematic drawing of the energy transfer process between identical quantum dots \((R_D = R_A)\).

In the initial state of the system the electron of the donor is in an excited state (in conduction band), the electron of the acceptor is in the ground state (in the valence band). As a result of the Coulomb interaction of the donor and acceptor electrons, the system passes in the final state where the electron of the acceptor is in a conduction band of the acceptor, in the donor the electron is in valence band.

### 2. Energy transfer matrix element

To obtain the rate of the nonradiative energy transfer between two quantum dots we need to calculate the energy transfer matrix element (the Coulomb interaction matrix element) for the system transition from the initial state to final state (see fig. 2). It can be expressed as

\[
M_{if} = \sum_{\sigma_1, \sigma_2} \int d^3r_1 d^3r_2 \Psi_f(\xi_1, \xi_2) \frac{e^2}{\epsilon |d + r_1 - r_2|} \Psi_i^*(\xi_1, \xi_2) \tag{1}
\]

where \(\xi_i = (r_i, \sigma_i)\), \(\sigma_1\) are spin variables, \(r_1\) and \(r_2\) are the radius-vectors of electrons in the donor and acceptor, respectively, measured from the center of the corresponding quantum dot. The antisymmetric wave functions of the initial and final states of the system under consideration are given by

\[
\Psi_i(\xi_1, \xi_2) = \frac{1}{\sqrt{2}} (\Psi_{cD}(r_1)\chi_{cD}(\sigma_1)\Psi_{hA}(r_2)\chi_{hA}(\sigma_2) - \Psi_{cD}(r_2)\chi_{cD}(\sigma_2)\Psi_{hA}(r_1)\chi_{hA}(\sigma_1)) \tag{2}
\]

\[
\Psi_f(\xi_1, \xi_2) = \frac{1}{\sqrt{2}} (\Psi_{hD}(r_1)\chi_{hD}(\sigma_1)\Psi_{cA}(r_2)\chi_{cA}(\sigma_2) - \Psi_{hD}(r_2)\chi_{hD}(\sigma_2)\Psi_{cA}(r_1)\chi_{cA}(\sigma_1)) \tag{3}
\]
Here \( \Psi_{cD}(r_1) \) and \( \Psi_{hD}(r_1) \) are the electron and hole spatial wave functions of the donor (similarly of the acceptor); \( \chi(\sigma) \) are the spin wave functions. Substituting wave functions (2) and (3) in the expression for the Coulomb interaction matrix element (1) results in dividing it into two terms:

\[
M_{if} = M_{coul} - M_{ex}
\]

where \( M_{coul} \) is the matrix element of the direct Coulomb interaction and \( M_{ex} \) is the matrix element of the exchange interaction. The matrix element of the direct Coulomb interaction for the system of two quantum dots is considered in detail in our previous work [10]. As present study focuses on the energy transfer by the exchange mechanism here we treat the matrix element of the exchange interaction that is of the form:

\[
M_{ex} = \int d^3r_1d^3r_2\Psi_{cD}^*(r_1)\Psi_{cA}(r_1)\frac{e^2}{|d + r_1 - r_2|}\Psi_{hD}(r_2)\Psi_{hA}^*(r_2)\times
\]

\[
× \sum_{\sigma_1,\sigma_2} \chi_{hD}(\sigma_2)\chi_{cA}(\sigma_1)\chi_{cD}(\sigma_1)\chi_{hA}(\sigma_2)
\]

Equation (5) determines the following selection rules in the exchange matrix element: \( M_{ex} \) is not equals to 0 when \( \chi_{cD} = \chi_{cA} \) and \( \chi_{hD} = \chi_{hA} \). However \( \chi_{cD}(D,A) \) is not necessary equal to \( \chi_{h(D,A)} \) so that the spin function on both quantum dots may change simultaneously. Ignoring the \( \chi \)'s, one can see that this integral represents the electrostatic interaction between two charge clouds \( Q_e(r_1) = e\Psi_{cD}^*(r_1)\Psi_{cA}(r_1) \) and \( Q_h(r_2) = e\Psi_{hA}^*(r_2)\Psi_{hD}(r_2) \).

3. Charge carrier wave functions

As it is known the Kane model provides the most adequate description of the energy spectra and wave functions of semiconductors A3B5 [11]. In this model the electron and hole wave functions can be written as

\[
\Psi = \Psi_s + \Psi_p
\]

where \( |s\rangle \) and \( |p\rangle \) are Bloch wave functions. The s-type functions describe the states in the conduction band; the p-type functions describe the states in the valence band. Kane's equations for the envelope functions and their solutions within the quantum dot and under the barrier are obtained in spherical approximation in [12]. In the consideration of the exchange interaction contribution in the energy transfer we have restricted ourselves to the calculations of the matrix element \( M_{ex} \) with the electron wave function \( \Psi_s |s\rangle \) that does not contain an admixture of the p-states and one of two heavy hole wave functions \( \Psi_{h1} |p\rangle \) where

\[
\Psi_s = Ajj(k_cr)V_{jm}(\theta,\phi)
\]

\[
\Psi_{h1} = A_1jj(k_hr)Y^j_{jm}(\theta,\phi)
\]

Here \( Y^j_{jm}(\theta,\phi) \) are the spherical functions, \( Y^j_{jm}(\theta,\phi) \) are the vector spherical harmonics, \( j \) and \( m \) are the angular momentum and its projection on z axis, respectively; \( jj(k_cr) \) are the spherical Bessel functions, where \( k_c \) and \( k_h \) are the wave numbers for the electrons and holes, respectively; and \( A_1 \) are normalizing constants. The corresponding wave functions under the barrier are used in the calculations.

4. Exchange interaction matrix element

Restricting ourselves to the calculations of the matrix element \( M_{ex} \) with the electron wave function \( \Psi_s |s\rangle \) (7) and the heavy hole wave function \( \Psi_{h1} |p\rangle \) (8), we obtain the estimation of the contribution of the exchange interaction in the energy transfer rate from below.
Considering only the coordinate part in the Eq. (6) and denoting $\Psi_s$ and $\Psi_{h1}$ functions for the donor and the acceptor by $\Psi_{csD}, \Psi_{csA}$ and by $\Psi_{hD}, \Psi_{hA}$ respectively, we can write the matrix element as follows:

$$M_{ex} = \int d^3r_1 d^3r_2 \Psi_{csD}^*(r_1) \Psi_{csA}(r_1) \frac{e^2}{\varepsilon |d + r_1 - r_2|} \Psi_{hD}(r_2) \Psi_{hA}(r_2). \tag{9}$$

In order to calculate the matrix element we place the origin of the coordinates in the center of the quantum-dot acceptor. In this coordinate system Eq. (9) may be rewritten as

$$M_{ex} = \int d^3r_1' d^3r_2' \Psi_{csD}^*(r_1' - d) \Psi_{csA}(r_1') \frac{e^2}{\varepsilon |r_1' - r_2'|} \Psi_{hD}(r_2 - d) \Psi_{hA}(r_2). \tag{10}$$

For the sake of simplicity of the calculations, we set values of the spherical functions and the vector spherical harmonics to be equal to their values at $\theta_1 = 0$, $\theta_2 = 0$, $\phi_1 = \pi$ and $\phi_2 = \pi$ that are determined by the angular moments and their projections on z axis as follows:

$$Y_{jm}(0, \phi) = \delta_{m0} \sqrt{\frac{2j + 1}{4\pi}},$$

$$Y_{jm}(\pi, \phi) = (-1)^j \delta_{m0} \sqrt{\frac{2j + 1}{4\pi}},$$

$$Y_{jm}^j(0, \phi) = \begin{cases} -m \sqrt{\frac{2j + 1}{8\pi}} \delta_{m0} e_m, & m = \pm 1 \\ 0, & \text{in the other cases.} \end{cases} \tag{11}$$

$$Y_{jm}^j(\pi, \phi) = (-1)^j Y_{jm}^j(0, \phi).$$

It should be noted that this approximation allows the calculations only for $m_{cD} = m_{cA} = 0$ and $m_{hD} = m_{hA} = \pm 1$. At other values of the full angular moment projections on z axis, the more exact $Y_{jm}(\theta, \phi)$ and $Y_{jm}^j(\theta, \phi)$ should be taken into account. The problem may be conveniently solved in the cylindrical coordinate system, as the system of two quantum dots treated has the axis connecting their centers. In this case the z-depending part of the donor electron wave functions in the donor range and under the barrier can be written as

$$\phi_{csD}(d - z_1') = A_{cD} j_{j_cD}(k_{cD}(d - z_1')), \quad d - R_D \leq z_1' \leq d;$$

$$\phi_{csD}(d - z_1') = B_{cD} k_{j_cD}(\kappa_{cD}(d - z_1')), \quad 0 \leq z_1' \leq d - R_D. \tag{12}$$

Boundary conditions for the functions are of the form:

$$A_{cD} j_{j_cD}(k_{cD}R_D) = B_{cD} k_{j_cD}(\kappa_{cD}R_D) \tag{13}$$

The z-depending parts of the acceptor electron wave functions, of the donor and acceptor hole wave functions and the boundary conditions for the functions can be written similarly. When calculating $M_{ex}$ we do not take into account the z-depending part of the electron and hole wave functions at $z_1' < 0$ and $z_1' > d$ because the modified spherical Bessel function $k_{j}(x)$ decays rapidly with increasing $x$. In the cylindrical coordinate system the Coulomb potential of the system under study is given by

$$\frac{e^2}{\varepsilon} = \frac{e^2}{\varepsilon \sqrt{p^2 + z^2}}. \tag{14}$$
The nonradiative energy transfer rate is determined by the Fermi golden rule as
\[ W_{\text{ex}} = W_{\text{coul}} + W_{\text{ex}} \]
where the density of final states \( \rho = \frac{1}{\pi} \), half-width of the energy level \( \Gamma = \frac{\hbar}{\tau} \), \( \tau \) - the lifetime of the electron-hole pair. The equation (18) is applicable only when interaction between charge carriers in QDs is weak. This means that energy level width is much larger than the transfer rate. In our calculations we took the radiative lifetime as \( \tau_1 = \text{inverse charge carrier lifetime} \). In the case of strong interaction, it is necessary to use density matrix formalism [13]. Because the contributions of the direct Coulomb and exchange interactions between the quantum-dot donor and the quantum-dot acceptor are independent the total energy transfer rate is given by
\[ W_{\text{ex}} = W_{\text{coul}} + W_{\text{ex}} \]
where \( W_{\text{coul}} \) is the rate of direct Coulomb transfer obtained in [10], \( W_{\text{ex}} \) is the rate of the exchange energy transfer.
Numerical calculations of exchange energy transfer rate (that is, the rate of energy transfer by Dexter mechanism) are carried out using expressions (19), (15), (12) and (13) for the case $R_D = R_A = R$ and taking into account the similar expressions for the $z$-depending parts of the acceptor electron wave functions, of the donor and acceptor hole wave functions and the boundary conditions for the functions. The basic transition in the quantum dots is considered. The dependencies of $W_{ex}$ on the distance $d$ are found for different values of the quantum dot radius $R$. The obtained dependences of $W_{ex}$ on the distance $d$ indicate that they are dominated by the electron and hole wave functions in the range under the barriers, which are the modified Bessel functions. The different decay rates of $W_{ex}$ are related to changing barrier height with radius of the quantum dot. A comparison between the values of $W_{ex}$ and $W_{coul}$ [10] at distances approaching to the contact ones shows that the contribution of the exchange interaction in the energy transfer should be taken into consideration in numerical calculations.

In conclusions, the results are useful in the correct interpretation of experimental data taking into account both the direct Coulomb interaction of the donor and acceptor electrons and their exchange interaction. This is of particular impotence for measurements of small distance within the biomolecule [2–4].

**Figure 3.** Calculus results of distance dependence of the energy transfer rate at the different quantum dot radii, radiative lifetime is $\tau = 10^{-9}$ s.

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