Resonance electronic excitation energy transfer in the quantum dot system

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Abstract

Microscopic theory of the nonradiative energy transfer in a system of III-V semiconductor quantum dots is elaborated in our work. The energy transfer both due to direct Coulomb and due to exchange interactions between two quantum dots (energy donor and acceptor) is considered. An analysis of energy transfer process is performed in the frame of the Kane model that provides the most adequate description of the real energy spectra and wave functions of III-V semiconductors. The density-matrix method is applied, which enabled us to analyze the energy transfer rate both in the weak-interaction approximation and in the strong-interaction approximation. For the first time the detailed analytical calculations of the exchange energy transfer rate for the quantum dot system are performed. The analytical expressions for contributions to the transfer rate are derived. The numerical calculations showed that at nearly contact distances between two quantum dots the rate of the energy transfer due to the direct Coulomb interaction as well as by exchange interaction can reach the saturation. At the small distances, these two contributions can be of the same order and can have the same value in the saturation range. It is revealed that the exchange interaction should be taken into consideration in qualitative describing the energy transfer at small distances between the quantum dot donor and the quantum dot acceptor.

Introduction

The electronic excitation energy transfer between quantum systems is one of the most important fundamental problems of modern physics. The phenomenon consists in that the electronic excitation energy is transferred from an energy donor [atom, molecule, semiconductor quantum dot (QD) or quantum well (QW)] to an energy acceptor. The following energy transfer mechanisms are distinguished: well-known radiative mechanism (when the donor emits a photon and the acceptor it then absorbs (see, e.g., 2, 3), nonradiative mechanism (in which energy is transferred from a donor to an acceptor via a single-step mechanism
in contrast to the radiative energy transfer\(^4\) and electron transfer mechanism (when an excited electron is transferred from the energy donor to the acceptor)\(^6\). The last two mechanisms quench the luminescence from a donor, but the first of these leads to a sensitized fluorescence of the acceptor, and the second yields a positively charged donor and a negatively charged acceptor (pairs of ions in the case of molecules). These mechanisms are fundamentally different: the nonradiative energy transfer occurs due to the Coulomb interaction of electrons of the energy donor and acceptor, whereas the electron transfer is only determined by the overlapping of the wave functions of the corresponding states of the donor and acceptor.

The nonradiative energy transfer was first observed in 1923 in experiments on the sensitized fluorescence of atoms in the gas phase\(^7\). Later, experiments of this kind were performed for molecule vapors\(^8\), liquid solutions of dyes\(^9\)–\(^11\), and solid solutions of organic molecules\(^12\). In parallel, a multitude of studies revealed the part played by the nonradiative energy transfer in biological systems (photosynthesis, in particular)\(^13\) (see also references in\(^14\)). Subsequently, the method based on the energy transfer between molecules of organic dyes found wide use in biological and medical experiments (see, e.g.,\(^15\)–\(^16\)).

In systems including semiconductor QDs, the nonradiative energy transfer was first observed in 1996\(^17\) and then started to be intensively studied both experimentally\(^18\) and theoretically\(^19\)–\(^22\). The interest is primarily due to the fact that the application of QDs has extended the potential of biological and medical experiments, both \textit{in vivo} and \textit{in vitro}, owing to their unique optical properties (narrow luminescence spectra, possibility of changing the spectral characteristics of QDs by varying their size due to the quantum confinement effect). Together with the optical characteristics, QDs have advantages for the photostability and chemical stability over organic dyes conventionally used in this area of research. The QD-based resonance energy transfer and its growing application in biology are overviewed in\(^23\). Representative examples of biological experiments based on the energy transfer between QDs are presented in review\(^24\). With particular interest in biosensing application, the
foundational and theoretical works on the energy transfer between QDs are discussed in overview. The extensive review on energy transfer with semiconductor quantum dot bioconjugates is presented in. Recent papers exhibited in these reviewers demonstrate that an investigation of nonradiative resonance energy transfer remains the topical problem until the preset time.

The possibility of technical applications of the mechanism of nonradiative energy transfer between QDs for constructing fast quantum computers, QD semiconductor lasers, and solar cells is discussed in the literature, which also stimulates studies of this physical process. In the development of the optoelectronic devices, the considerable attention is presently given to the exploiting of the densely packed thin QD films, which needs the consideration of the peculiarities of the energy transfer at small QDs separation.

The first quantum-mechanical description of the nonradiative energy transfer was developed by Forster for molecular systems. He assumed that the energy transfer mostly occurs as a result of the dipole-dipole interactions between molecules. Then, the theory was extended by Dexter via inclusion of the dipole-quadrupole and exchange interactions. Because the exchange interaction is only determined by the Coulomb interaction and by the spatial overlapping of wave functions of donor and acceptor carriers, the exchange mechanism allows energy transfer in those cases when the direct transfer is forbidden by selection rules. It was shown that the exchange contribution to the nonradiative energy transfer rate may be important in two cases: (i) when the distance between a donor and an acceptor is short and the wave functions are not strongly localized and (ii) when dipole-dipole transitions in the acceptor are forbidden by selection rules. In the last case, the exchange contribution becomes of key importance. By the example of a typical pair of impurities in neighboring lattice cells of a NaCl crystal, a value of $10^{12} - 10^{13} \text{s}^{-1}$ was obtained for the Coulomb contribution to the energy transfer rate, and a value smaller by one to two orders of magnitude, $10^{10} - 10^{11} \text{s}^{-1}$, for the exchange contribution.

In the Forster–Dexter theory, the nonradiative energy transfer is considered for the case
of a "very weak interaction" between an energy donor and acceptor in terms of the quantum-mechanical perturbation theory. Later, the method of density matrices was suggested, which can analyze various approximations in the energy-transfer theory and is applicable in the case of a strong interaction between a donor and an acceptor. The already performed theoretical considerations and experimental studies suggest that the energy transfer between molecules has been sufficiently examined.

The theory of the nonradiative resonance energy transfer in systems including semiconductor quantum structures has been insufficiently developed so far and is the subject of present-day studies. In,\textsuperscript{33} the nonradiative resonance energy transfer was first considered for a hybrid nanostructure constituted by a semiconductor QW and a layer of an organic acceptor. An analysis in the effective mass approximation for describing a Wannier–Mott exciton in a semiconductor QW and a making macroscopic electrodynamic description of the organic medium demonstrated the high efficiency of the nonradiative energy transfer from an exciton to an organic molecule, with the possible subsequent emission of light. The authors predicted the possibility of using hybrid structures of this kind for optical pumping of organic emission sources. Then, the same theoretical approach was used to analyze the mechanism of the nonradiative resonance energy transfer from a semiconductor QD to an organic matrix.\textsuperscript{34} It was shown that the transfer of a considerable part of energy from a QD to the surrounding optically active organic molecules is possible in this mechanism. The authors of this study noted that this effect will be manifested more clearly under electrical pumping of a QD, compared with the optical pumping. In,\textsuperscript{35–38} the theory of energy transfer in semiconductor–organic medium hybrid structures was further developed. The nonradiative energy transfer in another hybrid system, QD + protein molecule, was considered in\textsuperscript{39} by using the density-matrix formalism.

The mechanism of the nonradiative energy transfer between QDs has been studied with the use of various theoretical approaches: tight-binding method,\textsuperscript{19} method of a semi-empirical pseudopotential,\textsuperscript{20} and simple effective mass model.\textsuperscript{21,22} It was shown in\textsuperscript{19,20} that
the dipole-dipole approximation of the Coulomb interaction of electrons in a donor QD and an acceptor QD provides an adequate description of the nonradiative energy transfer process in the case of direct-gap semiconductors, and the dependence of the transfer rate $W$ on the distance $d$ between the QDs is described by a simple law $W \sim 1/d^6$. The contributions from higher multipoles are negligible down to the contact distances between the donor and acceptor. For indirect-gap semiconductors, the multipole terms are more important, but the dipole-dipole contributions remain dominant. The authors of\textsuperscript{21} found that the dipole-dipole contribution to the energy transfer rate is, as a rule, larger than the dipole-quadrupole contribution. However, the dipole-quadrupole contribution, which depends on the distance between the QDs as $1/d^8$, should be taken into account in a quantitative description at small distances comparable with the QD size. It was shown in\textsuperscript{22} that the dipole-dipole approximation is valid for describing the energy transfer for dipole-allowed transitions in the donor and acceptor for all distances between the QDs, down to nearly contact distances. It was also demonstrated that the rate of energy transfer from a donor to an acceptor, which corresponds to dipole-forbidden transitions in the acceptor, is also important and its contribution at nearly contact distances may reach a value of 25% relative to the contribution of the transfer for a dipole-allowed transition. When studying the energy transfer between QDs, the authors of\textsuperscript{22} neglected the exchange interaction by considering it insignificant and disregarded the admixture of valence-band states to the conduction band states (neglected the nonparabolicity effect). However, we demonstrated in the study reported here that the contribution of the exchange interaction to the nonradiative energy transfer should be taken into consideration in the case of nearly contact distances between a donor and an acceptor. It is noteworthy that the results of\textsuperscript{12–22} are in agreement at large donor–acceptor distances and show a significant discrepancy at small distances. In these studies, the rate of the resonance energy transfer is described within the framework of the first-order perturbation theory. In\textsuperscript{40} the generalized modeling Hamiltonian was used to formulate a model that made it possible to examine the influence exerted by the Stark effect on the resonance energy transfer between
QDs under the action of a short laser pulse. The dynamics variation of the occupation of the donor and acceptor levels was analyzed in relation to time and analytical expressions were derived for the excitation transfer rate at a constant resonance detuning and at a linear-time variation of the Stark shift of levels with consideration for the relaxation of the states via emission of phonons and photons. In\textsuperscript{41} the Foster energy transfer process is investigated with consideration for the nonradiative and radiative contributions in the context of the first order perturbation theory, where the electrostatic dipole-dipole coupling between the donor and the acceptor as well as their electromagnetic interaction is taken into account. It is demonstrated that for typical parameters of semiconductor quantum dots the efficiency of the nonradiative transfer is close to the unity at the small donor-acceptor separation and for the energy detuning not larger than 1-2 meV and decreases rapidly with an increase in the separation and the energy detuning. The radiative correction starts to play role only at relatively long separations greater than 40 nm.

Forster-type energy transfer in assemblies of arrayed nanostructures is analyzed in the work.\textsuperscript{42} Authors developed generalized theory for the nonradiative energy transfer in arrays with mixed dimensionalities. The processes of energy transfer from a single nanostructure (nanoparticle, nanowire, or quantum well) to 1D, 2D or 3D assemblies of nanoparticles and nanowire are studied paying particular attention to the functional distance dependence of the transfer rate. It is shown that the dependence is determined by the quantum confinement as well as array stacking dimensionality of the acceptor. It is found that distance dependence of the transfer rate changes from $d^{-6}$ to $d^{-5}$ when the acceptor nanoparticles are arranged in a 1D stack, and to $d^{-4}$ when in a 2D array, and to $d^{-3}$ when in a 3D array, whereas the rate distance dependence for acceptor nanowires changes from $d^{-5}$ to $d^{-4}$ when they are arranged in a 1D stack, and to $d^{-3}$ when in a 2D array. It should be noted that the above-mentioned theoretical studies consider the resonance energy transfer due to direct Coulomb interaction between quantum dots only and not taken into account their exchange interaction.

In paper\textsuperscript{43} the mechanism of exciton tandem tunneling is proposed. The corresponding
rate for exciton hops as well as the Dexter (exchange) rate and the Forster one are evaluated for epitaxially connected nanocrystals. Evaluations carried out give the exciton hop rate larger than the Dexter rate and for Si even larger than the Forster rate.

In the present communication, we suggest a microscopic theory of the mechanism by which the nonradiative resonance energy transfer occurs between spherical QDs based on a III–V semiconductor. Both the direct Coulomb and the exchange energy transfer mechanisms are considered. To our knowledge, the detailed theoretical study of the nonradiative energy transfer between semiconductor quantum dots by the exchange mechanism is not presented in the literature. The analytical treatment and numerical calculations of the exchange energy transfer rate for quantum dot system are first performed in our study. We used the density-matrix method that enabled us to carry out an energy transfer analysis both in the weak-interaction approximation, where the first order perturbation theory may be applied, and in the strong-interaction approximation. The previously employed models give no way of taking into account the real spectrum of III–V semiconductors and a number of the related new effects. We use the Kane model as the model the most adequately describing the real spectrum of III–V semiconductors. We found the selection rules determining the dipole-allowed and dipole-forbidden transitions in the acceptor and the dipole-allowed transition in the donor at which the energy-transfer matrix element is nonzero. It is shown that taking into account the real band structure of the semiconductors extends the class of dipole-allowed and dipole-forbidden transitions that are active in the energy transfer. The rates of both the direct Coulomb and the exchange energy transfer processes are calculated by using the density-matrix formalism. For all the contributions, the dependence of the transfer rate on the distance between the energy donor and acceptor are found. It is shown that at small distances the contribution of the exchange interaction between electrons in the donor and acceptor becomes important.

It is assumed that the donor QD and the acceptor QD are fabricated from the same III–V semiconductor compound and are embedded in the matrix of another material that creates
finite-depth potential wells for electrons \( (V_{cD}, V_{cA}) \) and holes \( (V_{hD}, V_{hA}) \). The subscripts D and A correspond to the donor and acceptor. The system of two QDs under consideration is shown in Fig. 1. Figures 2 and 3 show schematically the processes of the direct Coulomb and the exchange energy transfer, respectively. In the initial state of the system, the electron in the donor is in the excited state (in the conduction band), and the electron in the acceptor is in the ground state (in the valence band). As a result of both the direct Coulomb and the exchange interaction of the QDs, the excitation energy of the donor is transferred to the acceptor, and the system comes into the final state in which the electron in the donor is in the valence band and the electron in the acceptor is in the conduction band. Also noteworthy is that the nonradiative energy transfer process is similar to the Auger recombination in a QD, we considered previously in. However, in contrast to the Auger recombination in which the interacting electrons are localized within a QD, the energy transfer occurs as a result of interaction between electrons localized in different QDs, energy donor and acceptor.

![Figure 1: Diagram of two QDs: donor of radius \( R_D \) and acceptor of radius \( R_A \).](image)

**Theory**

**Energy transfer matrix element**

To determine the rate of the nonradiative energy transfer between two QDs, it is necessary to calculate the energy transfer matrix element (i.e., the matrix element of the Coulomb interaction) for the transition of the system from the initial to the final state (see Fig. 2).
Figure 2: Schematic of the energy transfer process in a two-quantum-dot system due to the direct Coulomb interaction

Figure 3: Schematic of the energy transfer process in a two-quantum-dot system due to the exchange interaction

It can be expressed as

$$M_{if} = \sum_{\sigma_1, \sigma_2} \int d^3r_1 d^3r_2 \psi_f^{*}(\xi_1, \xi_2) \frac{e^2}{\varepsilon |d + r_1 - r_2|} \psi_i(\xi_1, \xi_2),$$  \hspace{1cm} (1)$$

where $\xi_i = (r_i, \sigma_i)$, $r_1$ and $r_2$ are the radius-vectors of electrons in the donor and acceptor, respectively, measured from the center of the corresponding QD; $\sigma_i$ are spin variables; $\varepsilon$ is the static dielectric constant of the medium. The antisymmetrized wave functions of the...
initial and final states of the system under consideration are given by the expressions

\[\psi_i(\xi_1, \xi_2) = \frac{1}{\sqrt{2}} \left( \psi_{cD}(r_1)\chi_{cD}(\sigma_1)\psi_{hA}(r_2)\chi_{hA}(\sigma_2) - \psi_{cD}(r_2)\chi_{cD}(\sigma_2)\psi_{hA}(r_1)\chi_{hA}(\sigma_1) \right),\]

\[\psi_f(\xi_1, \xi_2) = \frac{1}{\sqrt{2}} \left( \psi_{hD}(r_1)\chi_{hD}(\sigma_1)\psi_{cA}(r_2)\chi_{cA}(\sigma_2) - \psi_{hD}(r_2)\chi_{hD}(\sigma_2)\psi_{cA}(r_1)\chi_{cA}(\sigma_1) \right),\]

(2)

Here, \(\psi_{cD}(r_i)\) and \(\psi_{hD}(r_i)\) are the wave functions of the spatial coordinates for electrons and holes in the donor (the functions for the acceptor can be written similarly), and \(\chi(\sigma_i)\) are spin wave functions. Substitution of wave functions (2) into the expression for matrix element (1) of the Coulomb interaction results in its separation into two terms:

\[M_{if} = M_{\text{coul}} - M_{\text{ex}}\]  (3)

where \(M_{\text{coul}}\) is the matrix of the direct Coulomb interaction, and \(M_{\text{ex}}\) is the matrix element of the exchange interaction. These matrix elements have the form

\[M_{\text{coul}} = \int d^3r_1 d^3r_2 \psi_{cD}(r_1)\psi_{cD}^*(r_1)\psi_{hD}^*(r_2)\psi_{hD}(r_2)\frac{e^2}{|d + r_1 - r_2|} \times \sum_{\sigma_1, \sigma_2} \chi_{hD}(\sigma_1)\chi_{cA}^*(\sigma_2)\chi_{cD}(\sigma_1)\chi_{hA}(\sigma_2),\]  (4)

and

\[M_{\text{ex}} = \int d^3r_1 d^3r_2 \psi_{cD}(r_1)\psi_{cD}^*(r_1)\psi_{hA}^*(r_2)\psi_{hA}(r_2)\frac{e^2}{|d + r_1 - r_2|} \times \sum_{\sigma_2, \sigma_1} \chi_{hD}(\sigma_2)\chi_{cA}^*(\sigma_1)\chi_{cD}(\sigma_1)\chi_{hA}(\sigma_2).\]  (5)

It follows from (4) that \(M_{\text{coul}}\) is nonzero only for the transitions in which all spins remain unchanged, i.e., \(\chi_{cD} = \chi_{hD}\) and \(\chi_{cA} = \chi_{hA}\). Equation (5) determines other selection rules: \(M_{\text{ex}}\) is not zero if \(\chi_{cD} = \chi_{cA}\) and \(\chi_{hD} = \chi_{hA}\). However, \(\chi_{c(D,A)}\) should not be equal to \(\chi_{h(D,A)}\)
and, consequently, the spin functions on both QDs may vary simultaneously. Ignoring the spin functions $\chi$ in (5), we can see that this integral represents the electrostatic interaction between two clouds of charges, $Q_c = e\psi^*_c(r_1)\psi_c(r_1)$ and $Q_c = e\psi^*_h(r_2)\psi_h(r_2)$.

**Carrier wave functions**

In this study, we consider the nonradiative resonance energy transfer between spherical QDs fabricated from III–V semiconductors. The most adequate description of the energy spectrum and wave functions of III–V semiconductors is provided by the Kane model. In this model, the electron and hole wave functions can be written as

$$\psi = \psi_s \, |s\rangle + \psi \, |p\rangle$$

where $|s\rangle$ and $|p\rangle$ are the Bloch wave functions of s- and p-types. Functions of the s-type describe states in the conduction band, and p-type functions describe states in the valence band. The functions $\psi_s$ and $\psi$ are envelope functions. In the spherical approximation, the Kane equations for the envelope functions have the form:

$$\begin{align*}
(E_g + \delta - E)\psi_s - i\hbar\gamma\nabla \psi &= 0, \\
- E\psi - i\hbar\gamma\nabla \psi_s + \frac{\hbar^2}{2m} (\gamma_1 + 4\gamma_2)\nabla (\nabla \psi) - \\
- \frac{\hbar^2}{2m} (\gamma_1 - 2\gamma_2)\nabla \times (\nabla \times \psi) + i\delta\sigma \times \psi &= 0,
\end{align*}$$

where $\delta = \frac{\Delta_{so}}{3}$ ($\Delta_{so}$ is the spin-orbit coupling constant), $\gamma$ is the Kane matrix element having the rate dimension and related to the matrix element of the momentum operator between states of the conduction band and valence band, $\gamma_1$ and $\gamma_2$ are generalized Luttinger parameters, and $m$ is the free electron mass. Below, we consider the case in which the spin-orbit coupling constant $\Delta_{so} = 0$. Later, we discuss the effect of the spin-orbit coupling on the energy transfer process. Solutions to the Kane equations were also obtained in. The
envelope functions of electrons within a QD are represented by the expressions:

\[
\psi_s = A j_j(k_c r) Y_{jm}(\theta, \phi),
\]

\[
\psi = -\frac{i \hbar \gamma}{E_c + E_g} A k_c \left( \sqrt{\frac{j + 1}{2j + 1}} j_{j+1}(k_c r) Y_{jm}^{j+1}(\theta, \phi) + \right.
\]
\[
+ \sqrt{\frac{j}{2j + 1}} j_{j-1}(k_c r) Y_{jm}^{j-1}(\theta, \phi) \right).
\]

Here, \(Y_{jm}(\theta, \phi)\) are spherical functions; \(Y_{jm}^{j+1}(\theta, \phi)\) and \(Y_{jm}^{j-1}(\theta, \phi)\) are vector spherical harmonics; \(j\) and \(m\) are values of the full angular momentum and its projections on the \(z\) axis, respectively; \(j_j(k_c r)\) are spherical Bessel functions, where \(k_c\) is the wave number for the electron, \(E_g\) is the energy gap width; \(E_c\) is the electron energy reckoned from the conduction band bottom; and \(A\) is a normalizing constant. The envelope functions for electrons under the barrier:

\[
\psi_s = B k_j(\kappa_c r) Y_{jm}(\theta, \phi),
\]

\[
\psi = -\frac{i \hbar \gamma \nabla \psi_s}{\bar{E} + \bar{E}_g}
\]

\[
\nabla \psi_s = B \kappa_c \left( -\sqrt{\frac{j + 1}{2j + 1}} k_{j+1}(\kappa_c r) Y_{jm}^{j+1} + \right.
\]
\[
+ \sqrt{\frac{j}{2j + 1}} k_{j-1}(\kappa_c r) Y_{jm}^{j-1} \right),
\]

\[
\bar{E}_g = E_g + V_c + V_v,
\]

\[
\bar{E}_c = E_c - V_c.
\]

Here, \(k_j(\kappa_c r)\) is the modified spherical Bessel function, \(\kappa_c\) is the pseudowave number, \(B\) is a normalizing constant, and \(\bar{E}_c\) is the electron energy reckoned from the conduction band bottom in the wide-bandgap region.

In the three-band Kane model, the states of heavy holes are doubly degenerate because the spin-split band merges with the band of heavy holes. The corresponding wave functions \(\psi_{h1}\) and \(\psi_{h2}\) contain no \(\psi_s\) component and have different polarizations, which are determined
by the polarizations of the vector spherical harmonics:

\[
\psi_{h1} = A_1 j_j(k_h r) Y_{jm}^j(\theta, \phi),
\]

\[
\psi_{h2} = A_2 \left( \sqrt{\frac{j}{2j+1}} j_j(k_h r) Y_{jm}^{j+1}(\theta, \phi) - \sqrt{\frac{j+1}{2j+1}} j_{j-1}(k_h r) Y_{jm}^{j-1}(\theta, \phi) \right),
\]

where \( k_h \) is the wave number of a hole, and \( A_1 \) and \( A_2 \) are normalization constants. The wave functions of heavy holes under the barrier were found in the form:

\[
\psi_{h1} = B_1 k_j(\kappa_h r) Y_{jm}^j(\theta, \phi),
\]

\[
\psi_{h2} = B_2 \left( \sqrt{\frac{j}{2j+1}} k_j(\kappa_h r) Y_{jm}^{j+1}(\theta, \phi) - \sqrt{\frac{j+1}{2j+1}} k_{j-1}(\kappa_h r) Y_{jm}^{j-1}(\theta, \phi) \right).
\]

In the Kane model, the principal quantum numbers \( n_c \) and \( n_h \) are introduced as \( n \)-th root of the dispersion relationship for electrons and holes, respectively. The dispersion relationship has the form

\[
j_j(k_c R) \left[ \kappa_c \tilde{Z} \left( \frac{j k_j(\kappa_c R)}{\kappa_c R} - k_{j+1}(\kappa_c R) \right) \right] = \]

\[
= k_j(\kappa_c R) \left[ k_c \tilde{Z} \left( \frac{j j_j(\kappa_c R)}{k_c R} - j_{j+1}(\kappa_c R) \right) \right],
\]

Here, \( Z = 1/(\mathcal{E} + E_g) \) to the left of the barrier, \( \tilde{Z} = 1/(\mathcal{E} + E_g + V_v) \) to the right of the barrier, and \( \mathcal{E} \) is the electron energy reckoned from the conduction band bottom. The wave number \( k_c \) and the pseudo-wave number \( \kappa_c \) are given by

\[
k_c^2 = \frac{\mathcal{E}(\mathcal{E} + E_g)}{\hbar^2 \gamma^2}
\]
and
\[ \kappa_h^2 = \left( V_c - \phi \right) \frac{\left( \epsilon + E_g + V_v \right)}{\hbar^2 \gamma^2}. \]
\hspace{1cm} (14)

The dispersion relationship for holes has the form
\[ j_j(k_h R) \frac{\kappa_h}{k_h} \left[ j_j \left( \frac{j+1}{\kappa_h R} \right) - k_{j+2}(\kappa_h R) \right] + 
+ (j+1) \left( \frac{(j-1)k_{j-1}(\kappa_h R)}{\kappa_h R} - k_j(\kappa_h R) \right) = 
\]
\[ = k_j(\kappa_h R) \frac{k_h}{\kappa_h} \left[ j_j \left( \frac{(j+1)k_{j+1}(\kappa_h R)}{k_h R} - j_{j+2}(\kappa_h R) \right) - 
- (j+1) \left( \frac{(j-1)k_{j-1}(\kappa_h R)}{k_h R} - j_j(\kappa_h R) \right) \right], \]
\hspace{1cm} (15)
(21) where the wave number \( k_h \) and the pseudo-wave number \( \kappa_h \) for holes
\[ k_h^2 = -2 \frac{m_h E_h}{\hbar^2}, \]
\hspace{1cm} (16)
\[ \kappa_h^2 = 2 \frac{m_h (V_v - E_h)}{\hbar^2}. \]
\hspace{1cm} (17)

The quantum-confinement levels for electrons and holes are determined by equations (12) and (15), together with the dispersion laws for electrons and holes.\(^{46}\)

**Matrix element of direct Coulomb interaction**

Because the matrix element of the direct Coulomb interaction contains the Coulomb interaction operator dependent on the variables \( \mathbf{r}_1 \) and \( \mathbf{r}_2 \), it is convenient, in order to separate the integration over these variables, to use the representation of the Coulomb interaction via the Fourier integral:
\[ \frac{e^2}{\varepsilon |\mathbf{d} + \mathbf{r}_1 - \mathbf{r}_2|} = 
\]
\[ = \frac{1}{2\pi^2 \varepsilon} \int d^3q \frac{1}{q^2} \exp(i \mathbf{q} \cdot (\mathbf{d} + \mathbf{r}_1 - \mathbf{r}_2)). \]
\hspace{1cm} (18)
Then, the matrix element takes the form

\[ M_{\text{coul}} = \frac{1}{2\pi^2\varepsilon} \int d^3 q \exp(iq \cdot d) \frac{1}{q^2} I_D(q) I_A^*(q), \]  

(19)

where the overlapping integrals for the donor and acceptor take the following form

\[ I_D = \int d^3 r_1 \exp(iq \cdot r_1) \psi_{cD}(r_1) \psi_{hD}^*(r_1), \]
\[ I_A = \int d^3 r_2 \exp(iq \cdot r_2) \psi_{cA}(r_2) \psi_{hA}^*(r_2). \]

(20)

Our consideration is performed in the framework of the Kane model, and, therefore, we take into account the admixture of valence band and conduction band states. The electron wave function contains both the s- and p-components [see (6)]; the heavy hole wave functions contain only the p-component.

To derive an expression for the integral \( I_{D1} \) without consideration for the mixing-in of valence band and conduction band states, the following should be performed. First, we use the long-wavelength approximation by assuming that \( qa \ll 1 \) (\( a \) is the lattice constant), which makes it possible to separate the integration over the rapidly oscillating Bloch function and the slowly varying envelope function. Further, it can be noted that the first term in the Taylor series expansion of the exponential gives no contribution to the overall integral because the conduction-band and valence-band functions are orthogonal. Therefore, the contribution is made by the second term in the expansion, which takes the form

\[ I_{D1} \approx \int d^3 r_1 \psi_{hD}^*(r_1) \psi_{cSD}(r_1) \exp(iqr_1) \langle p | iqr_1 | s \rangle. \]

(21)

The integral \( I_{D1} \) is proportional to the matrix element of the coordinate operator, \( \langle p | r_\alpha | s \rangle \), which can be expressed through the parameters of the semiconductor\(^47\)

\[ \langle s | z | Z \rangle = \frac{P}{E_g}. \]

(22)
Here, $Z$ is one of the Bloch functions of the valence band (the others are $X$, $Y$). These functions are transformed as the corresponding coordinates, and $P = \hbar \gamma$ is the Kane parameter related to the matrix element of the momentum operator between the states of the conduction band and valence band. For simplicity and convenience of further calculations, we considered the crystallographic axes in the QDs to be codirectional, which results in that the full matrix element is independent of the mutual orientation of the dipole momenta. If the angular dependence and the averaging over angles are taken into account, a factor of $2/3$ appears in the matrix element. Therefore, the integral $I_{D1}$ can be written as

$$I_{D1} = i \frac{P}{E_g} \int d^3 r_1 (\mathbf{q} \cdot \psi^*_{hD}(\mathbf{r}_1)) \psi_{cSD}(\mathbf{r}_1) \exp(i\mathbf{q}\mathbf{r}_1).$$

(23)

Because we assume in our model that $\Delta_{so} = 0$, heavy holes are doubly degenerate. By virtue of this circumstance, there appear two different matrix elements corresponding to transitions involving heavy holes with various polarizations. Let us designate the matrix element corresponding to transitions of holes with the first and second polarizations as $M_{coul}^{(1)}$ and $M_{coul}^{(2)}$, respectively. Calculations for the matrix element are made in section "Calculation of direct-Coulomb matrix element". Except for the matrix elements for the direct Coulomb interaction involving a heavy hole with the first or second polarization, two additional contributions for each polarization of heavy holes appear in the full matrix element for the direct Coulomb interaction. We name these contributions the mixed-in contributions. One of these is the contribution associated with only the mixing-in, and the second is the cross contribution. These contributions appear because the overlapping integral for the donor and acceptor [formula (20)] contains a full electron wave function in the Kane model, which is a superposition of the envelope function and s-type Bloch function and also of the envelope (vector) function and p-type Bloch function. This representation results in that two terms appear in each overlap integral, and just this circumstance leads to the appearance of the above contributions. A detailed calculation of these contributions
was made in a separate communication. The admixture contribution was considered and it was shown that the contribution from these matrix elements is 5–10 times smaller than the contribution disregarding the admixture. Let us now calculate the above matrix elements $M_{\text{Coul}}^{(1)}$ and $M_{\text{Coul}}^{(2)}$. The selection rules for the matrix element $M_{\text{Coul}}^{(1)}$ have the form:

$$
\begin{align*}
    m_{cA} &= m_{hA}, \\
    m_{cD} &= m_{hD}, \\
    l_1 + j_{cD} + j_{hD} - &\text{even}, \\
    l_2 + j_{cA} + j_{hA} - &\text{even}, \\
    |l_1 - j_{cD}| &\leq j_{hD} \leq l_1 + j_{cD}, \\
    |l_2 - j_{cA}| &\leq j_{hA} \leq l_2 + j_{cA}.
\end{align*}
$$

(24)

The selection rules (24) follow from the symmetry properties of the Klebsch–Gordan coefficients [section “Calculation of direct-Coulomb matrix element”, (62)]. In the case of $l_1 = 0$ and $l_2 = 0$, we obtain the following simplified expression for the matrix element

$$
M_{\text{Coul}}^{(1)} = \frac{e^2}{\varepsilon D} \mathcal{B}_{DA}^{(1)} \int_0^{R_D} \int_0^{R_A} r_1^2 dr_1 r_2^2 dr_2 \times
$$

$$
\times (j_{cD}(k_{cD}r_1)j_{hD}(k_{hD}r_1))(j_{cA}(k_{cA}r_2)j_{hA}(k_{hA}r_2)) \times
$$

$$
\times \sqrt{\frac{2j_{cD} + 1}{2j_{hD} + 1}} \sqrt{\frac{2j_{cA} + 1}{2j_{hA} + 1}} C^{j_{hD}.m_{hD}}_{j_{hA} m_{hA},1,0} C^{j_{hA}.m_{hA}}_{j_{hA} m_{hA},1,0} \times
$$

$$
\times \delta_{j_{cD}j_{hD}} \delta_{m_{cD}m_{hD}} \delta_{j_{cA}j_{hA}} \delta_{m_{cA}m_{hA}},
$$

(25)

where

$$
\mathcal{B}_{DA}^{(i)} = 2 \left( \frac{P}{E_g} \right)^2 A_{cDA}A_{hDA}A_{cA}A_{hA}, \ i = 1, 2.
$$

(26)

It follows from the selection rules (24) for the matrix element that the matrix element is not zero at $l_1 = l_2 = 0$ for transitions involving electrons and holes with equal angular momenta $j_{cD} = j_{hD}$ and $j_{cA} = j_{hA}$. These transitions are dipole-allowed. It follows for this case from
expression (25) that the energy-transfer matrix element depends on the donor–acceptor distance as \( M^{(1)}_{\text{Coul}} \sim 1/d^3 \). If \( l_1 + l_2 \) is odd, the sums of the angular momenta \( j_{cD} + j_{hD} \) and \( j_{cA} + j_{hA} \) of the states involved in the dipole transition must have the opposite parity. The minimum admissible values of \( l_1 \) and \( l_2 \) are, respectively, 0 and 1. In this case, the restrictions imposed on the allowed angular momenta in (24) have the form \( j_{cD} = j_{hD} \) and \( |1 - j_{cA}| \leq |1 + j_{cA}| \). Accordingly, the contribution to the matrix element of the Coulomb interaction can only be made in the acceptor by dipole-forbidden transitions. When the above conditions are satisfied, \( M^{(1)}_{\text{Coul}} \) depends on the donor–acceptor distance as \( 1/d^4 \). It is clear that, for the transition to be possible, it is necessary that the transition energies in the donor and acceptor, which depend on the QD radii \( R_D \) and \( R_A \) should coincide. In the case of the identical radii of QDs having the same system of energy levels, it is clear that the resonance energy transfer becomes possible only when all the quantum numbers are the same. Let us now consider the matrix element for a heavy hole with the second polarization. This matrix element is also calculated in section "Calculation of direct-Coulomb matrix element" [formula (73) and onward].

The symmetry properties of the Klebsch–Gordan coefficients\(^{49}\) give selection rules for the matrix element \( M^{(2)}_{\text{Coul}} \) (73):

\[
\begin{align*}
    m_{cA} &= m_{hA}, \\
    m_{cD} &= m_{hD}, \\
    l_1 + j_{cD} + j_{hD} &= \text{odd}, \\
    l_2 + j_{cA} + j_{hA} &= \text{odd}, \\
    |l_1 - j_{cD}| &\leq j_{hD} \pm 1 \leq l_1 + j_{cD}, \\
    |l_2 - j_{cA}| &\leq j_{hA} \pm 1 \leq l_2 + j_{cA}, \\
    \text{also, } j_{hD}, j_{hA} &\geq 1.
\end{align*}
\]
If \( l_1 + l_2 = 0 \), expression (73) is simplified to take the form

\[
M^{(2)}_{\text{coul}} = \frac{e^2}{\varepsilon d^3} B^{(2)}_{DA} \int_0^{R_D} r_1^2 dr_1 \int_0^{R_A} r_2^2 dr_2 \times
\]

\[
\times \left( j_{c,D}(k_{c,D}r_1) \left( \sqrt{\frac{j_{h,D}}{2j_{h,D}+1}} j_{h,D}+1(k_{h,D}r_1)C^{j_{h,D},m_{h,D}}_{j_{h,D}+1,m_{h,D},1,0} \times \right.ight.
\]

\[
\left. \left. \times \delta_{j_{c,D}j_{h,D}+1}\delta_{m_{c,D},m_{h,D}} - \sqrt{\frac{j_{h,D}+1}{2j_{h,D}+1}} j_{h,D}-1(k_{h,D}r_1) \times \right. \right.
\]

\[
\left. \left. \times C^{j_{h,D},m_{h,D}}_{j_{h,D}-1,m_{h,D},1,0}\delta_{j_{c,D}j_{h,D}-1}\delta_{m_{c,D},m_{h,D}} \right) \right) \times \right.
\]

\[
\times \left( j_{c,A}(k_{c,A}r_2) \left( \sqrt{\frac{j_{h,A}}{2j_{h,A}+1}} j_{h,A}+1(k_{h,A}r_2)C^{j_{h,A},m_{h,A}}_{j_{h,A}+1,m_{h,A},1,0} \times \right.ight.
\]

\[
\left. \left. \times \delta_{j_{c,A}j_{h,A}+1}\delta_{m_{c,A},m_{h,A}} - \sqrt{\frac{j_{h,A}+1}{2j_{h,A}+1}} j_{h,A}-1(k_{h,A}r_2) \times \right. \right.
\]

\[
\left. \left. \times C^{j_{h,A},m_{h,A}}_{j_{h,A}-1,m_{h,A},1,0}\delta_{j_{c,A}j_{h,A}-1}\delta_{m_{c,A},m_{h,A}} \right) \right). \tag{28}\]

It follows from the selection rules (27) that the matrix element is not zero at \( l_1 = l_2 = 0 \) only for the dipole-forbidden transitions in the donor and acceptor, when the conditions \( j_{c,D} = j_{h,D} \pm 1 \) and \( j_{c,A} = j_{h,A} \pm 1 \) are satisfied. For this case, the matrix element \( M^{(2)}_{\text{coul}} \) depends on the donor–acceptor distance as \( 1/d^3 \). When \( l_1 + l_2 \) is an odd number with the minimum possible values \( l_1 = 0 \) and \( l_2 = 1 \), the matrix element is nonzero for the dipole-forbidden transitions in the donor if the condition \( j_{c,D} = j_{h,D} \pm 1 \) is satisfied; the following constraints are imposed on the transitions in the acceptor: \( j_{c,A} + j_{h,A} \) is an even number and \( |1 - j_{c,A}| \leq j_{h,A} \pm 1 \leq 1 + j_{c,A} \). When the above conditions are satisfied, the matrix element \( M^{(2)}_{\text{coul}} \) depends on distance \( d \) as \( 1/d^4 \). As already noted, for the matrix element to be nonzero, the relative values of \( R_D \) and \( R_A \) should provide the resonance conditions for the corresponding transitions. In the case of QDs with the same radii, the resonance is observed for transitions between levels with coinciding angular momenta, for electrons and holes of both QDs.
Matrix element of exchange interaction

When analyzing the contribution of the exchange interaction to the energy transfer, we restricted our consideration to a calculation of the matrix element $M_{ex}$ with electron wave function $\psi_s$ (8) and heavy hole wave function $\psi_{h1}$ (10). Thus, we obtained the lower-bound estimate for the contribution of the exchange interaction to the energy transfer rate.

Considering only the coordinate-related part in (5) and designating the functions $\psi_s$ and $\psi_{h1}$ for the donor and acceptor as $\psi_{csD}$, $\psi_{csA}$ and $\psi_{hD}$, $\psi_{hA}$, respectively, we can write the matrix element $M_{ex}$ as:

$$M_{ex} = \int d^3r_1' \int d^3r_2 \psi_{csD}(r_1)\psi_{csA}^*(r_1) \frac{e^2}{\varepsilon |d + r_1 - r_2|} \times$$

$$\times \psi_{hD}^*(r_2)\psi_{hA}(r_2)$$

(29)

It is noteworthy that the radius vector $r_1$ is reckoned from the donor center in the wave function of the donor, and $r_2$, from the acceptor center in the wave function of the acceptor. To calculate the matrix element, we place the origin of coordinates at the center of the acceptor QD. In this coordinate system, (29) can be rewritten as

$$M_{ex} = \int d^3r_1' \int d^3r_2 \psi_{csD}(r_1' - d)\psi_{csA}^*(r_1') \frac{e^2}{\varepsilon |r_1' - r_2|} \times$$

$$\times \psi_{hD}^*(r_2 - d)\psi_{hA}(r_2)$$

(30)

To simplify the calculation, we assume that the values of the spherical functions and vector spherical harmonics are equal to their values at $\theta_1 = 0$, $\theta_2 = 0$, $\theta_1' = \pi$ and $\theta_2' = \pi$, which
are determined by the angular momenta $J$ and their projections on the $z$ axis:

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

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

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

(31)

It should be noted that this approximation enables calculations only for $m_{cD} = m_{cA} = 0$ and $m_{hD} = m_{hA} = \pm 1$. At other projections of the angular momentum on the axis, the more precise $Y_{jm}(\theta,\phi)$ and $Y^j_{jm}(\theta,\phi)$ should be taken into account.

It is convenient to solve our problem in the cylindrical system of coordinates because the system of two QDs under consideration has an axis that connects the QD centers. In the cylindrical system of coordinates, the $z$-dependent parts of the donor electron wave functions in the donor region and under the barrier can be written as

$$\phi_{csD}(d - z'_1) = A_{cD} j_{cD}(k_{cD}(d - z'_1)), \quad d - R_D \leq z'_1 \leq d,$$

$$\phi_{csD}(d - z'_1) = B_{cD} k_{cD}(\kappa_{cD}(d - z'_1)), \quad 0 \leq z'_1 \leq d - R_D.$$  

(32)

The boundary conditions for these functions have the form

$$A_{cD} j_{cD}(k_{cD} R_D) = B_{cD} k_{cD}(\kappa_{cD} R_D).$$

(33)

The $z$-dependent parts of the acceptor electron wave functions, donor and acceptor hole wave functions, and the boundary conditions for these functions can be written in a similar way. In the cylindrical system of coordinates, the Coulomb potential of the system under
consideration is represented by the expression
\[
\frac{e^2}{\varepsilon r} = \frac{e^2}{\varepsilon \sqrt{p^2 + z^2}}.
\] (34)

Here, \( r = |\mathbf{r}_1' - \mathbf{r}_2|, z = z_1' - z_2, p^2 = \rho_1^2 + \rho_2^2 - 2\rho_1\rho_2 \cos(\varphi_1 - \varphi_2) \). Using the integral formula
\[
\frac{1}{\sqrt{p^2 + z^2}} = \int_0^\infty e^{-q|z|}J_0(qp)\,dq,
\] (35)

where \( J_0(qp) \) is the zero-order Bessel function, we can rewrite the matrix element as
\[
M_{ex} \approx \frac{e^2}{\varepsilon} S \int \rho_1 d\rho_1 d\varphi_1 dz_1' \int \rho_2 d\rho_2 d\varphi_2 dz_2 \times
\int_0^\infty dq \phi_{csD}(d - z_1')\phi_{csA}^*(z_1') \times
\times \exp(-q|z_1' - z_2|)J_0(qp)\phi_{hD}^*(d - z_2)\phi_{hA}(z_2).
\] (36)

The quantity \( S \) is represented by the expression
\[
S = (-1)^{j_{cD} + j_{hD} + m_{hD} + 1}\delta_{m_{cD},0} \sqrt{\frac{2j_{cD} + 1}{4\pi}} \times
\times \delta_{m_{cA},0} \sqrt{\frac{2j_{cD} + 1}{4\pi}} \times
\times (\delta_{m_{hD},1} + \delta_{m_{hD},-1}) \sqrt{\frac{2j_{hD} + 1}{8\pi}} \sqrt{\frac{2j_{hA} + 1}{8\pi}} \delta_{m_{hD},m_{hA}}.
\] (37)

In accordance with Graf’s summation theorem, \( J_0(qp) \) can be represented as
\[
J_0(qp) = \sum_{n=-\infty}^{\infty} J_n(qp_1)J_n(qp_2)e^{in(\varphi_1 - \varphi_2)},
\] (38)

where the variables \( \rho_1, \rho_2, \varphi_1, \varphi_2 \) are separated. Substituting this expression in (36), we
Figure 4: Dependence of the rate of direct Coulomb energy transfer on the distance between the QDs. The calculation was made for donor and acceptor transitions with quantum numbers $n_c = n_h = 1$ for the wave function of heavy holes with the second polarization, $\psi_{h2}$, for the ground transition. The following radii were used $R_D = R_A = 2, 2.5$ nm. $M^{(2)}_{coul}$ was calculated for the values of the angular momentum and its projection $(0,0)$ and $(1,0)$. The transverse relaxation time was taken to be $T_2 = 10^{-11}$ s.

Bring the matrix element to the form

$$M_{ex} \approx \frac{e^2}{\varepsilon} 4\pi^2 S \int \rho_1 d\rho_1 dz'_1 \int \rho_2 d\rho_2 dz_2 \times$$
$$\times \int_0^{\infty} dq \phi_{csD}(d - z'_1)\phi_{csA}^*(z'_1) \exp(-q|z'_1 - z_2|) \times$$
$$\times J_0(q\rho_1)J_0(q\rho_2)\phi_{hD}^*(d - z_2)\phi_{hA}(z_2),$$

(39)

because all the integrals over $\varphi_1$ and $\varphi_2$ are zero for all $n$ except $n = 0$. The integration range over $\rho$ is determined by the approximation chosen for the functions $Y_{jm}(\theta, \phi)$ and $\mathbf{Y}_{jm}^j(\theta, \phi)$.
Figure 5: Dependence of the rate of direct Coulomb energy transfer on the distance between the QDs. The calculation was made for donor and acceptor transitions with quantum numbers \( n_c = n_h = 1 \) for the wave function of heavy holes with the second polarization, \( \psi_{h2} \), for the ground transition. The following radii were used \( R_D = R_A = 2, 2.5 \) nm. \( M^{(2)}_{\text{coul}} \) was calculated for the values of the angular momentum and its projection \((0,0)\) and \((1,0)\). The transverse relaxation time was taken to be \( T_2 = 10^{-12} \) s.

, i.e., by the condition \( \rho_{\text{max}} \ll d \). To calculate the integrals take over \( \rho \) in (39), it is useful to employ the following representation:\(^{50}\)

\[
\int_0^{\rho_{\text{max}}} \rho_1(2) J_0(q\rho_1(2)) d\rho_1(2) = \frac{\rho_{\text{max}}}{q} J_1(q\rho_{\text{max}}). \tag{40}
\]
As a result, the matrix element can be obtained in the form

\[
M_{\text{ex}} \approx e^2 \varepsilon 4\pi^2 S\rho_{\text{max}}^2 \int_0^\infty dq \frac{J^2_1(q\rho_{\text{max}})}{q^2} \times \\
\times \int dz'_1 \int dz_2 \phi_{csD}(d - z'_1)\phi^*_c(z'_1) \times \\
\times e^{-q|z'_1 - z_2|}\phi_{hD}(d - z_2)\phi_{hA}(z_2).
\]

Integration in (40) over \( q \) yields:

\[
\int_0^\infty dq \frac{J^2_1(q\rho_{\text{max}})}{q^2} \exp(-q|z'_1 - z_2|) = \\
= \rho_{\text{max}} \left\{ \frac{4}{3\pi}(\eta^2 + 1)^{1/2} \left[ \eta^2 K\left( (\eta^2 + 1)^{-1/2}\right) \right] + \\
+ (1 - \eta^2)E\left( (\eta^2 + 1)^{-1/2}\right) \right\} - \eta \right\}.
\]

Here, \( \eta = (|z'_1 - z_2|)/(2\rho_{\text{max}}) \), \( K(\xi) \) and \( E(\xi) \) are full elliptical integrals of the first and second order. Let us introduce the following quantities

\[
P(\eta_{1(2)}) = \rho_{\text{max}} \left\{ \frac{4}{3\pi}(\eta_{1(2)}^2 + 1)^{1/2} \times \\
\times \left[ \eta_{1(2)}^2 K\left( (\eta_{1(2)}^2 + 1)^{-1/2}\right) + (1 - \eta_{1(2)}^2)E\left( (\eta_{1(2)}^2 + 1)^{-1/2}\right) \right]\right\},
\]

where \( \eta_1 = (z'_1 - z_2)/(2\rho_{\text{max}}) \) for \( z'_1 > z_2 \) and \( \eta_2 = (z_2 - z'_1)/(2\rho_{\text{max}}) \) for \( z_2 > z'_1 \). Then,
matrix element (41) can be rewritten as

\[
M_{ex} \approx \frac{e^2}{\varepsilon} 4\pi^2 S \rho_{\text{max}}^3
\]

\[
\begin{align*}
&\left[ \int_0^R_A \phi_{csD}^*(d - z_1') \phi_{csA}(z_1') dz_1' + \int_{R_A}^{d-R_D} \phi_{csD}(d - z_1') \phi_{csA}^*(z_1') dz_1' + \\
&\int_0^d \phi_{csD}(d - z_1') \phi_{csA}^*(z_1') dz_1' \right] \cdot \left[ \int_0^{z_1'} \phi_{cD}^*(d - z_2) \times \\
&\phi_{hA}(z_2)(P(\eta_2^2) - \eta_1) dz_2 + \\
&\int_z^{d} \phi_{cD}^*(d - z_2) \phi_{hA}(z_2)(P(\eta_2^2) - \eta_2) dz_2 \right] \\
&\equiv \frac{e^2}{\varepsilon} 4\pi^2 S \rho_{\text{max}}^3 [J_1 + J_2 + J_3]
\end{align*}
\] (44)

The \( J_1, J_2, \) and \( J_3 \) determine the contributions to the matrix element from the acceptor region, region between the QDs, and donor region, respectively. In its turn the quantity \( J_1 \) can be written as

\[
J_1 = \int_0^{R_A} \phi_{csD}(d - z_1') \phi_{csA}^*(z_1') dz_1' \left[ \int_0^{z_1'} \phi_{cD}^*(d - z_2) \phi_{hA}(z_2) \left( P(\eta_2^2) - \eta_1 \right) dz_2 + \\
\int_{z_1'}^{d} \phi_{cD}^*(d - z_2) \phi_{hA}(z_2) \left( P(\eta_2^2) - \eta_2 \right) dz_2 + \\
\int_{R_A}^{d} \phi_{cD}^*(d - z_2) \phi_{hA}(z_2) \left( P(\eta_1^2) - \eta_1 \right) dz_2 \right].
\] (45)

A detailed calculation of the integrals in (45) is made in section "Calculation of exchange integrals". The integrals appearing in \( J_2, J_3 \) are calculated in a similar manner. As a result of the cumbersome manipulations, the exchange interaction matrix element (44) is obtained.
in the following form:

\[
M_{ex} \approx \frac{e^2}{\varepsilon} 2\pi^2 S \rho^3 \sin(k_c D R_D) \left( \frac{\sin(k_{hD} R_D)}{k_{hD} R_D} - \cos(k_{hD} R_D) \right) \times \\
\times \frac{1}{k_c A} \frac{1}{k_{cD} d} \frac{1}{k_{hA}} \frac{1}{k_{hD} d} \exp(- (\kappa_{cD} + \kappa_{hD})(d - R_D - R_A)).
\]

(46)

Energy transfer probability

Let us now consider the problem of calculating the rate of the nonradiative resonance energy transfer between QDs, i.e., the probability of transfer in unit time. We consider the energy transfer from a donor QD (D) to an acceptor QD (A). In what follows, we are interested in the process of energy transfer in a system with irreversible energy transfer from the donor QD to the acceptor QD, associated with the relaxation of excited states. To describe the energy transfer in a quantum-mechanical system with dissipation, it is convenient to use the density-matrix method, which makes it possible to phenomenologically take into account both the relaxation processes within the system and the interaction of the quantum-mechanical system with its environment.\textsuperscript{1,52} The equation for the density matrix \( \hat{\rho} \) has in our case the following form:\textsuperscript{1,53}

\[
\begin{align*}
\frac{i\hbar}{\partial t} \rho_{jj} &= [M_c, \rho]_{jj} + \frac{i\hbar}{T_1} (\rho_{jj}^e - \rho_{jj}), \\
\frac{i\hbar}{\partial t} \rho_{ij} &= (E_i - E_j) \rho_{ij} + [M_c, \rho]_{ij} - \frac{i\hbar}{T_2} \rho_{ij}.
\end{align*}
\]

(47)

Here, \( M_c \) is the matrix element of the Coulomb interaction between the QDs, \( \rho_{ii} \) are diagonal elements of the density matrix, \( \rho_{ij} \) are its off-diagonal elements, \( \rho_{jj}^e \) is the equilibrium value of the diagonal element of the density matrix, \( T_1 \) is the "longitudinal" relaxation time of the diagonal elements of the density matrix (this the time of radiative and nonradiative transitions between levels, which determines the occupancy of states), \( T_2 \) is the "transverse" time characterizing the relaxation of the off-diagonal elements of the density matrix, and \( E_i - E_j \) is the energy difference between the initial and excited states.
Let us consider the density matrix for the following states (of the donor and acceptor):

\[ |1\rangle = \psi_D' \psi_A, \quad |2\rangle = \psi_D \psi_A', \quad |3\rangle = \psi_D \psi_A. \]

(48)

Here, the prime is related to the excited states of the donor and acceptor. The \(|3\rangle\) state in which both QDs are in the ground state (are not excited) is necessary for retaining the normalization: \(\rho_{11} + \rho_{22} + \rho_{33} = 1\). In our case (room temperature), the energy gap widths of the donor and acceptor QDs \(E_{gD,A} \gg k_B T\) (\(k_B\) is the Boltzmann constant, and \(T\) is absolute temperature). Then, it is apparent that the equilibrium values of the diagonal elements of the density matrix are given by \(\rho_{11}' = \rho_{22}' = 0, \rho_{33}' = 1\). As a result, we have from (47) a system of equations for the elements of the density matrix. \(^{1}\)

\[
\begin{align*}
\frac{\partial \rho_{11}}{\partial t} &= \frac{1}{i\hbar}((M_c)_{12}\rho_{21} - (M_c)_{21}\rho_{12}) - \frac{\rho_{11}}{\tau_D}, \\
\frac{\partial \rho_{22}}{\partial t} &= \frac{1}{i\hbar}((M_c)_{21}\rho_{12} - (M_c)_{12}\rho_{21}) - \frac{\rho_{22}}{\tau_A}, \\
\frac{\partial \rho_{12}}{\partial t} &= \frac{1}{i\hbar}(M_c)_{12}(\rho_{22} - \rho_{11}) - \frac{\rho_{12}}{T_2} + \frac{\Delta E}{i\hbar}\rho_{12}, \\
\frac{\partial \rho_{21}}{\partial t} &= \frac{1}{i\hbar}(M_c)_{21}(\rho_{11} - \rho_{22}) - \frac{\rho_{21}}{T_2} - \frac{\Delta E}{i\hbar}\rho_{21}.
\end{align*}
\]

(49)

Here, \(\Delta E = E_{gA} - E_{gD}\) (resonance detuning), \(\tau_D\) and \(\tau_A\) are the longitudinal relaxation times for the donor and acceptor; the transverse relaxation time for two interacting QDs (D and A) is related to halfwidths of levels in the donor and acceptor, \(\Gamma_D\) and \(\Gamma_A\), by \(\frac{1}{T_2} = \frac{\Gamma_D}{\hbar} + \frac{\Gamma_A}{\hbar}\).

Let us analyze the system of equations (47) following\(^{1}\). First, the general solution to system (49) has the nature of damped oscillations. Second, an excited donor can discharge energy (i.e., relax with a characteristic time \(\tau_l\)) via two processes: radiative recombination \(1/\tau_D\), or energy transfer to the acceptor, i.e.:

\[
\frac{1}{\tau_l} \equiv \left[ \int_0^{\infty} \rho_{11}(t) dt \right]^{-1} = \frac{1}{\tau_D} + \mathcal{W},
\]

(50)
Figure 6: Dependence of the rate of energy transfer by the exchange mechanism between two QDs. The calculations were made for principal quantum numbers of electrons and holes \( n_c = n_h = 1 \) and angular momenta \( j_c = 0 \) and \( j_h = 1 \). The following radii were used: (a) \( R_D = R_A = 2 \) nm, (b) \( R_D = R_A = 2.5 \) nm. The radiative lifetime was taken to be \( \tau_A = 10^{-9} \) s, and the transverse relaxation time, to be \( T_2 = 10^{-11} \) s

where \( \overline{W} \) can be regarded as a generalized probability of energy transfer from the donor to the acceptor. Further, let us solve the system of equations (50) by the method suggested in;\(^{54}\) for this purpose, we perform the Laplace transform of the density-matrix components:

\[
\begin{align*}
    f_{ij}(s) &= \mathcal{L}(\rho_{ij}) = \int_0^\infty \exp(-st)\rho_{ij}(t)dt, \\
    \int_0^\infty \exp(-st)\frac{\partial \rho_{ij}}{\partial t}dt &= sf_{ij}(s) - \rho_{ij}(0).
\end{align*}
\]
Figure 7: Dependence of the rate of energy transfer by the exchange mechanism on the donor and acceptor radius at a near contact distance \((d = 2R + 0.6 \text{ nm})\) between the QDs. The calculation was made for the principal quantum numbers of electrons and holes \(n_c = n_h = 1\) and angular momenta \(j_c = 0\) and \(j_h = 1\). The radiative lifetime was taken to be \(\tau_A = 10^{-9}\) s, and the transverse relaxation time, to be \(T_2 = 10^{-11}\) s.

As a result of the Laplace transform, the system of equations (50) becomes

\[
\begin{align*}
sf_{11} - \rho_{11}(0) &= \frac{1}{i\hbar}((Mc)_{12}f_{21} - (Mc)_{21}f_{12}) - \frac{f_{11}}{\tau_D}, \\
sf_{22} - \rho_{22}(0) &= \frac{1}{i\hbar}((Mc)_{21}f_{12} - (Mc)_{12}f_{21}) - \frac{f_{22}}{\tau_A}, \\
set_{12} - \rho_{12}(0) &= \frac{1}{i\hbar}(Mc)_{12}(f_{22} - f_{11}) - \frac{f_{12}}{T_2} + \frac{\Delta E}{i\hbar}f_{12}, \\
set_{21} - \rho_{21}(0) &= \frac{1}{i\hbar}(Mc)_{21}(f_{11} - f_{22}) - \frac{f_{21}}{T_2} - \frac{\Delta E}{i\hbar}f_{21}.
\end{align*}
\]

(52)

It should be noted that, according to (50) and (51), the generalized probability can be represented as

\[
\mathcal{W} = -\frac{1}{\tau_D} + f_{11}^{-1}(0),
\]

(53)

where

\[
f_{11}(0) = \int_0^\infty \rho_{11}(t)dt.
\]

(54)

Assuming that \(s = 0\) in (52) and taking into account the initial conditions \(\rho_{11}(0) = 1\) and
$\rho_{ij}(0) = 0$ at $i \neq 1$ or $j \neq 1$, we obtain the following solution:

$$f_{11}^{-1}(0) = \left[ \int_{0}^{\infty} \rho_{11}(t) dt \right]^{-1} =$$

$$= \frac{1}{\tau_D} + \frac{2|\langle M_c \rangle_{12}|^2 T_2/\hbar^2}{1 + \left( \frac{T_2 \Delta E}{\hbar} \right)^2 + \frac{2|\langle M_c \rangle_{12}|^2}{\hbar^2} T_2 \tau_A}.$$  

(55)

As a result, we have for the generalized transfer probability $\overline{W}$:

$$\overline{W} = \frac{2|\langle M_c \rangle_{12}|^2 T_2/\hbar^2}{1 + \left( \frac{T_2 \Delta E}{\hbar} \right)^2 + \frac{2|\langle M_c \rangle_{12}|^2}{\hbar^2} T_2 \tau_A}. \quad (56)$$

To analyze this solution and determine its physical meaning, let us consider a number of particular cases.

The first case corresponds to a small distance between the QDs, when their interaction is strong, so that

$$|M_c| \gg \frac{\hbar}{\tau_D}, \frac{\hbar}{\tau_A}, \frac{\hbar}{T_2}.$$  

(57)

In this case, solution (49) for $\rho_{11}$ (at $\Delta E = 0$) oscillates with frequency $\Omega = \frac{2|\langle M_c \rangle|}{\hbar}$; the energy transfer from the donor to the acceptor and back occurs in the system. In this limiting case, the generalized probability $\overline{W}$ tends to $1/\tau_A$; i.e., the energy transfer rate is determined by the rate at which the acceptor passes from the excited to the ground state.

At a weak interaction between the QDs, when $\frac{2|\langle M_c \rangle|^2}{\hbar^2} T_2 \tau_A \ll 1$, we have, according to (56):

$$\overline{W} = W = \frac{2|\langle M_c \rangle_{12}|^2 T_2/\hbar^2}{1 + \left( \frac{T_2 \Delta E}{\hbar} \right)^2}. \quad (58)$$

In this case, the energy transfer from a donor to an acceptor is an irreversible process and $W$ corresponds to the true probability of energy transfer in unit time. It should be noted that expression (58) can be derived in the framework of the ordinary perturbation theory.
Expression (58) can be rewritten as

\[ W = \frac{2\pi}{\hbar} |(M_c)_{12}|^2 \rho_f, \]  

(59)

where

\[ \rho_f = \frac{1}{\pi} \frac{T_2/\hbar}{1 + (T_2\Delta E)^2/\hbar^2}. \]  

(60)

Here, \( \rho_f \) has the meaning of the density of final states. Above, we calculated the matrix elements of the Coulomb interaction, which correspond to two polarizations of heavy holes \( [M_{\text{coul}}^{(1)} \text{ (62)} \text{ and } M_{\text{coul}}^{(2)} \text{ (73)}] \) and the exchange matrix element \( M_{\text{ex}} \) (44). The transitions involved in the energy transfer are determined by the corresponding selection rules. Because all these contributions are independent, the full probability of energy transfer from a donor QD to an acceptor QD is given by

\[ W_{D\rightarrow A} = \sum_{\alpha} W_{D\rightarrow A}^\alpha, \]  

(61)

where \( \alpha \) enumerates independent processes, and \( W_{D\rightarrow A}^\alpha \) corresponds to the transfer probability for each of these.

\section*{Results and discussion}

\subsection*{Direct Coulomb energy transfer}

When the direct Coulomb interaction is considered, the matrix element for a heavy hole with the second polarization, \( M_{\text{coul}}^{(2)} \), is taken into account because the transfer involving the ground state of the donor and acceptor for electrons and holes occurs just for this matrix element. The calculations were made for the donor and acceptor based on the InAs material in a GaAs matrix, with radii \( R_D = R_A = 2 \, \text{nm} \) and \( R_D = R_A = 2.5 \, \text{nm} \) for \( V_c = V_v = 0.52 \, \text{eV}, \ E_g = 0.38 \, \text{eV}, \ m_e = 0.03m_0, \ m_h = 0.5m_0. \) The calculation was performed for two
acceptor relaxation times $\tau_A = 10^{-9}$ s and $\tau_A = 10^{-10}$ s. The transverse relaxation time was taken to be $T_2 = 10^{-11}$ s (Fig. 4) and $T_2 = 10^{-12}$ s (Fig. 5). It should be noted that the electron lifetime in the ground state ($10^{-9}$ s) is in good agreement with the time obtained in.\textsuperscript{55,56} The experimental values of this time have been repeatedly reported. The authors of\textsuperscript{57} obtained a lifetime $\tau = 882$ ps. This value is very close to the radiative time $\tau = 0.7$ ns obtained in.\textsuperscript{58} The transverse relaxation time $T_2 = 10^{-11}$ s is close to the value obtained in.\textsuperscript{59,60} Nevertheless, we allow variations of these two times by assuming the possible differences in the structure of both the QD material itself and the embedding matrix.

The dependence of the energy transfer rate on the distance between the QDs, calculated by the formula for the generalized transfer probability (58), is shown in Figs. 4 and 5 for two values of $\tau_A$. It can be seen in the figures that the longer the acceptor lifetime, the larger the distance between the QDs at which the generalized probability $W_{coul}$ approaches a constant value (saturates). It can also be seen in Figs. 4 and 5 that, at large distances between the QDs, the generalized probability can be described by a formula of the perturbation theory, and hence follows that the probability of the Coulomb transfer obeys the $1/d^6$ law at large distances, as follows from the Forster theory. The transfer rate at contact distances is determined as the inverse lifetime in the acceptor. Note that the direct Coulomb energy transfer matrix elements are calculated based on the Kane model neglecting spin-orbit interaction. It was shown in\textsuperscript{48} that the inclusion of the spin-orbit interaction to the Kane model results in multiplication of the direct Coulomb energy transfer rate by the function $F(\Delta_{SO}/E_g)$, which changes weakly for any relation between $\Delta_{SO}$ and $E_g$, having a maximum value $F(\Delta_{SO}/E_g) = 1$ and minimum value $F(\Delta_{SO}/E_g) = 0.9$.

**Exchange energy transfer**

Numerical calculations of the exchange energy transfer rate were performed for InAs QDs in a GaAs matrix with the same radii $R_D = R_A$ of 2 and 2.5 nm. The same parameters of the system were used as those in calculations of the energy transfer via a direct Coulomb
interaction: \( V_c = V_v = 0.52 \, eV, \, E_g = 0.38 \, eV, \, m_e = 0.03m_0, \, m_h = 0.5m_0 \). The transitions between the energy levels in the donor and acceptor with principal quantum numbers \( n_c = n_h = 1 \), angular momenta \( j_c = 0, \, j_h = 1 \), and their projections \( m_c = 0, \, m_h = 1 \) were considered. The matrix element of the exchange energy transfer was calculated by formula (44). The rate of the exchange energy transfer was found both by formula (56) for the generalized transfer probability \( W_{ex} \) and by formula (58) for the transfer probability \( W_{ex} \) at a weak interaction between the donor and acceptor. Two electron lifetimes in the ground state of the conduction band were taken (\( \tau_A = 10^{-9} \) s and \( \tau_A = 10^{-10} \) s) and two values of the transverse relaxation time were assumed (\( T_2 = 10^{-11} \) s or \( T_2 = 10^{-12} \) s).

Figure 6 shows how the exchange energy transfer rate depends on the distance \( d \) between the donor and acceptor for QDs with radii \( R_D = R_A = 2 \) nm. Calculations were made for the transverse relaxation time \( T_2 = 10^{-11} \) s and electron lifetime in the ground state of the conduction band \( \tau_A = 10^{-9} \) s. It can be seen that, at nearly contact distances \( d \), there is a noticeable difference between the transfer rate found from expression (56) for \( W_{ex} \) and the transfer rate found from expression (58) for \( W_{ex} \). \( W_{ex} \) exhibits saturation and tends to the rate of acceptor transition from the excited state to the ground state \((1/\tau_A)\). Consequently, the exchange interaction cannot be considered as weak in this case. At large distances \( d \), the rates \( W_{ex} \) and \( W_{ex} \) coincide. This indicates that the system parameters taken in our calculation satisfy the weak interaction condition \( 2|M_{ex}|^2 T_2 \tau_A/(\hbar^2) \ll 1 \) and formula (58) can be used to calculate the transfer rate. The dependence of the transfer rate at distances \( d \) exceeding the nearly contact distances exhibits an exponential behavior. Calculation shows that the difference between \( W_{ex} \) and \( W_{ex} \) at short \( d \) is substantially smaller for the electron lifetime \( \tau_A = 10^{-10} \) s.

For QDs with \( R_D = R_A = 2.5 \) nm, the dependences of \( W_{ex} \) and \( W_{ex} \) on distance \( d \) were calculated at the same transverse relaxation time \( T_2 = 10^{-11} \) s and the same electron lifetimes \( \tau_A = 10^{-9} \) s and \( \tau_A = 10^{-10} \) s. As shown by Fig. 7, the dependences of \( W_{ex} \) and \( W_{ex} \), obtained at \( \tau_A = 10^{-9} \) s, are exponential and nearly coincide in the whole range of
distances $d$. The dependences of $W_{ex}$ and $W_{ex}$ exhibit the same behavior at $\tau_A = 10^{-10}$ s. The exponential dependence obtained is consistent with the theoretical consideration for the exchange energy transfer between impurity atoms or ions in an insulating crystal under the assumption that the interaction is weak.\footnote{5} We can also note that experimental data for organic molecules is well described as the exchange energy transfer with the exponential dependence on the distance using Perrin approximation.\footnote{61}

The same behavior of the dependences of $W_{ex}$ and $W_{ex}$ was obtained on the assumption of a shorter transverse relaxation time $T_2 = 10^{-12}$ s at both times $\tau_A$ under consideration for QDs with both $R_D = R_A = 2$ nm and $R_D = R_A = 2.5$ nm.

Thus, in all the case under consideration, except the first case with $\tau_A = 10^{-9}$ s and $T_2 = 10^{-11}$ s, the system parameters taken in the calculation satisfy the weak interaction condition $2|M_{ex}|^2 T_2 \tau_A/(\hbar^2) \ll 1$ in the whole range of $d$ and formula (58) can be used to calculate the energy transfer rate.

Comparison of Fig. 4 for the rate of the direct Coulomb transfer and Fig. 6a for the rate of the exchange transfer between QDs with $R_D = R_A = 2$ nm shows that at small distances $d$, at which the rates of transfer by both mechanisms experience a saturation, the contributions of these two mechanisms to the total transfer rate are the same for the parameters chosen to be $\tau_A = 10^{-9}$ s and $T_2 = 10^{-11}$ s. The exchange transfer rate is an order of magnitude lower than the direct Coulomb transfer rate at $d = 5.2$ nm and is two orders of magnitude lower at $d = 5.7$ nm. Thus, the contribution of the exchange transfer to the total transfer rate should be taken into account in numerical calculations at nearly contact distances between the QDs. As the calculation demonstrated, the rate of the exchange transfer between QDs with $R_D = R_A = 2.5$ nm at the same $\tau_A = 10^{-9}$ s and $T_2 = 10^{-11}$ s for the contact distance $d$ is nearly an order of magnitude lower than that of the direct Coulomb transfer.

The dependence of the exchange energy transfer rate on the QD radius is determined by the quantum-confinement effect. It is known that, as the QD size increases, the energies of the ground and excited states of electrons and holes become lower. This leads to an increase
in the localizing potential and, as a consequence, to a weaker penetration of wave functions into the subbarrier region. As a result, the overlap integral of the wave functions of the donor and acceptor decreases and so does the energy transfer rate. Figure 7 shows the dependence of the energy transfer rate on the donor and acceptor radius \( R_D = R_A \), calculated for the minimum distance \( d \). It can be seen that an increase in the QD radius from \( R_D = R_A = 2.0 \) nm to \( R_D = R_A = 2.5 \) nm leads to a substantial decrease in the exchange transfer rate. The result is in agreement with data,\(^\text{62}\) where experiments revealed faster energy transfer rates in smaller QD donor sizes.

The energy-transfer analysis made here and the set of plots make it possible to optimize parameters of the QD system for observing the maximum effect.

**Conclusions**

A microscopic theory of the mechanisms of nonradiative energy transfer between semiconductor quantum dots (QDs) based on III–V compounds is developed in the framework of the three-band Kane model. Analytical expressions are derived both for the direct Coulomb interaction contributions and for the exchange interaction contributions to the energy transfer matrix element in a system of two spherical QDs fabricated from the same III–V semiconductor material and embedded in a matrix of another semiconductor material. According to the selection rules obtained in the study, the energy transfer process can involve both dipole-allowed and dipole-forbidden transitions in the donor and acceptor. In order to find the energy transfer rate, the density-matrix method is used. For the Coulomb interaction a numerical calculations of the generalized energy transfer rate for the lowest energy transition in the donor and acceptor demonstrate a saturation at the nearly contact distances between the donor and acceptor. This indicates that the Coulomb interaction cannot be considered as weak in this case. At larger distances \( d \) between the QDs, the rate of the direct Coulomb energy transfer obeys the \( 1/d^6 \) law in accordance with the Forster theory. The exchange en-
ergy transfer between QDs is first analyzed in detail. A numerical calculations show that the exchange energy transfer rate saturates at the nearly contact distances \( d \) between the donor and acceptor and becomes exponential as \( d \) increases. At the small distances, the contribution of the exchange interaction to the energy transfer rate may be of the same order of magnitude as the contribution of the direct Coulomb interaction and these contributions may have the same value in the saturation range. Consequently, it is important to take into account both of these contributions in a quantitative description of the energy transfer between QDs.

Two recent papers\textsuperscript{62,63} support our result that in the systems including QDs the exchange interaction can play a significant role in the energy transfer at small donor-acceptor separation. It is experimentally shown in\textsuperscript{62} that in the CdSe QD-Squaraine light harvesting assemblies, the exchange (Dexter) process is essential to the energy transfer and dominates the dipole-based Forster one at the smaller QDs. In\textsuperscript{63} the measured energy transfer rates in the close-packed blends of CdSe/CdZnS core/shell QDs are found to be more than an order of magnitude larger than the rate predicted by Forster theory, which cannot be satisfactory explained by several possible factors considered in the paper. We believe that exchange contribution to the energy transfer should be also taken into account for the consideration the discrepancy.

Thus our work enhances understanding of the features both of the direct coulomb and of the exchange energy transfer between quantum dots at their small separations. The results can be importance for the developing of the high-performance electronics based on thin films of the density packed QDs. Our results are also essential for the investigation of the structure of biomolecules and their complexes. The nonradiative energy transfer between the energy donor and acceptor conjugated with biomolecules is widely used in medical and biological experiments.\textsuperscript{23–26} The application of semiconductor QDs as both a donor and an acceptor improved the potentiality of these experiments. The high sensitivity of the transfer rate to changes in the distance between the energy donor and acceptor makes it possible
to detect the formation of antigen-antibody and enzyme-substrate complexes and the DNA hybridization and to study the structure and dynamics of biomolecules, where it is necessary to measure short distances within a molecule. Results of studies of this kind are highly important for diagnostics and therapy of a number of diseases, including those of oncological nature. The development of an adequate energy transfer theory taking into account both the direct Coulomb interaction between electrons of a donor and an acceptor and their exchange interaction is necessary for correct interpretation of experimental data.

**Calculation of direct-Coulomb matrix element**

To calculate the overlap integral $I_{D1}$ and then the matrix element, the following steps should be taken. In the first step, it is convenient to substitute the representation of the wave vector $q$ and the hole wave function in terms of the cyclic coordinates and then calculate the scalar product. In the second step, the plane wave is expanded in spherical functions. In the third step, it is necessary to perform integration over angular variables and substitute the results in the matrix element. So, we can represent the matrix element as

\[
M^{(1)}_{\text{coul}} = \frac{2e^2}{\pi \varepsilon} \left( \frac{P}{E_g} \right)^2 A_{cD} A_{h1D} A_{cA} A_{h1A} \times \\
\times \int_0^{R_D} r_1^2 dr_1 \int_0^{R_A} r_2^2 dr_2 \times \\
\times \frac{1}{3} \sum_{l_1, l_2 = 0}^{\infty} \left( j_{j_{cD}}(k_{cD} r_1) j_{j_{hD}}(k_{hD} r_1) \right) \times \\
\times \left( j_{j_{cA}}(k_{cA} r_2) j_{j_{hA}}(k_{hA} r_2) \right) \times \\
\times \sqrt{\frac{2j_{cD} + 1}{2j_{hD} + 1}} \sqrt{\frac{2j_{cA} + 1}{2j_{hA} + 1}} C^{j_{hA}}_{j_{hA}} C^{j_{hA}}_{j_{hA}} \times \\
\times (2l_1 + 1)(2l_2 + 1) r_1^{-l_1} r_2^{-l_2} C^{j_{hD},0}_{l_1,0,j_{cD},0} C^{j_{hD},m_{hD}}_{l_1,0,j_{cD},m_{hD}} \times \\
\times C^{j_{hA},0}_{l_2,0,j_{cA},0} C^{j_{hA},m_{hA}}_{l_2,0,j_{cA},m_{hA}} I(q),
\]

(62)
where

\[ I(q) = \int dq q^2 d\Omega_q \hat{n}_1(qr_1) \hat{n}_2(qr_2) \exp(\text{i}qd \cos(\theta_q)) \times (Y_{10}(\Omega_q))^2. \]  

(63)

Here, \( R_D \) and \( R_A \) are, respectively, the radii of the donor and acceptor QDs; \( A_{cD} \) and \( A_{h1D} \) are the normalization constants for the donor electron and hole wave functions (similarly for the acceptor); and \( k_{eD} \) and \( k_{hD} \) are the electron and hole wave numbers of the donor (similarly for the acceptor). It is noteworthy that integration only over the QD region in the matrix element is sufficient because the heavy hole wave function rapidly decays into the barrier. To integrate over \( q \) in (62), we are going to need a series expansion of the plane wave:

\[
\exp(\text{i}qd \cos(\theta_q)) = \sqrt{4\pi} \sum_{l=0}^{\infty} i^l j_l(qd) \sqrt{2l + 1} Y_{l0}(\Omega_q). 
\]

(64)

The product of two spherical functions is expressed as:

\[
(Y_{10}(\Omega_q))^2 = \sum_{LM} \sqrt{\frac{9}{4\pi(2L + 1)}} C_{1010}^{L0} C_{010}^{L0} Y_{LM}(\Omega_q).
\]

(65)

By virtue of the symmetry properties of the Clebsch–Gordan coefficients, only the coefficients with \( L = 0, 2 \) are nonzero in (65). In this case, \( l = L = 0, 2 \). Therefore, integral (63) can be represented as

\[ I(q) = \frac{1}{d^3} (I_0 - 2I_2), \]

(66)

where

\[ I_l = \int_0^\infty t^2 dt j_l(t) j_{l1}(t \frac{r_1}{d}) j_{l2}(t \frac{r_2}{d}); \]

(67)
and \( l \) takes two values: 0 and 2. Integral (6) can be expressed through the hypergeometric Appel function \( F_4(a, b; c, d; x, y) \).

\[
I_l = \pi \frac{3}{2} \left( \frac{r_1}{d} \right)^{l_1} \left( \frac{r_2}{d} \right)^{l_2} \times \\
\times \left[ \frac{\Gamma(l_1 + l_2 + l + 3)}{\Gamma(l_1 + \frac{3}{2}) \Gamma(l_2 + \frac{3}{2}) \Gamma(l + l_1 + l_2 + \frac{3}{2})} \times \\
F_4 \left( \frac{l_1 + l_2 - l + 2}{2}, \frac{l_1 + l_2 + l + 3}{2}; l_1 + \frac{3}{2}, l_2 + \frac{3}{2}; \left( \frac{r_1}{d} \right)^2, \left( \frac{r_2}{d} \right)^2 \right) \right],
\]

where \( \Gamma(x) \) is the gamma function. The calculated integral enters into expression (62) for the matrix element. It follows from the properties of the gamma function that the matrix element \( M_{Coul}^{(1)} \) is nonzero if one of the conditions

\[
\begin{cases}
1. l_1 = l_2 = 0, \\
2. l_1 + l_2 - \text{odd}.
\end{cases}
\]

is satisfied. Substituting (66) into (62), we obtain the matrix element

\[
M_{Coul}^{(1)} = \frac{2}{\pi} \frac{e^2}{\varepsilon d^3} \left( \frac{P}{E_g} \right)^2 A_{cD} A_{h1D} A_{cA} A_{h1A} \times \\
\times \int_{0}^{R_D} r_1^2 dr_1 \int_{0}^{R_A} r_2^2 dr_2 \times \\
\times \sqrt{2} \sum_{l_1,l_2=0}^{\infty} \left( j_{cD} (k_{cD} r_1) j_{hD} (k_{hD} r_1) \right) \times \\
\times \left( j_{cA} (k_{cA} r_2) j_{hA} (k_{hA} r_2) \right) \times \\
\times \sqrt{2j_{cD} + 1} \sqrt{2j_{cA} + 1} \sqrt{2j_{hD} + 1} \sqrt{2j_{hA} + 1} \times \\
\times (2l_1 + 1)(2l_2 + 1) i^{l_1 - l_2} C_{j_{hD},m_{hD}}^{j_{cD},m_{cD}} C_{j_{hD},m_{hD}}^{j_{cA},m_{cA}} \times \\
\times C_{l_2,j_{cA},m_{cA}}^{j_{hA},m_{hA}} C_{l_2,j_{cA},m_{cA}}^{j_{hA},m_{hA}} (I_0 - 2I_2).
\]

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When $l_1 = l_2 = 0$, it can be shown that

\begin{align*}
I_0 &= 0, \\
I_2 &= \pi^{3/2} \frac{1}{2} \frac{\Gamma(5/2)}{\Gamma(3/2) \Gamma(3/2) \Gamma(1)} = \frac{3\pi}{2}.
\end{align*}

(71)

and, therefore, the matrix element takes the form

\begin{align*}
M_{\text{coul}}^{(1)} &= 2 \frac{e^2}{\varepsilon d^3} \left( \frac{P}{E_g} \right)^2 A_{cD}A_{h1D}A_{cA}A_{h1A} \int_{0}^{R_D} r_1^2 dr_1 \int_{0}^{R_A} r_2^2 dr_2 \times \\
&\times \sum_{l_1, l_2=0}^{\infty} (j_{jcD}(k_{cD}r_1)j_{jhD}(k_{hD}r_1))(j_{jcA}(k_{cA}r_2)j_{jhA}(k_{hA}r_2)) \times \\
&\times \sqrt{\frac{2j_{cD}+1}{2j_{hD}+1}} \sqrt{\frac{2j_{cA}+1}{2j_{hA}+1}} C_{j_{hD}, m_{hD}}^{j_{hA}, m_{hA}, 1,0} C_{j_{hA}, m_{hA}}^{j_{hA}, m_{hA}, 1,0} \times \\
&\times (2l_1 + 1)(2l_2 + 1) \delta_{l_1-l_2} C_{l_1,0,j_{cD},0}^{j_{hD},m_{hD},0} C_{l_2,0,j_{cA},0}^{j_{hA},m_{hA},0} \times \\
&\times C_{l_1,0,j_{cD},0}^{j_{hA},m_{hA},0} C_{l_2,0,j_{cA},0}^{j_{hA},m_{hA},0}.
\end{align*}

(72)

Let us now consider the matrix element $M_{\text{coul}}^{(2)}$ with the wave function $\psi_{h2}$ of a heavy hole with the second polarization. This matrix element can be calculated similarly to the
matrix element \( M^{(1)}_{\text{Coul}} \) and has the form

\[
M^{(2)}_{\text{Coul}} = \frac{e^2}{\varepsilon d^3} \frac{2}{3\pi} \left( \frac{P}{E_g} \right)^2 A_{cD} A_{h2D} A_{cA} A_{h2A} \times \\
\times \int_0^{R_D} \int_0^{R_A} dr_1 r_1^2 dr_2 r_2^2 \sum_{l_1,l_2=0}^{\infty} (j_{j_{cD}}(k_{cD}r_1)) \times \\
\times \left( \sqrt{\frac{j_hD}{2j_{hD}+1}} j_{hD}+1(k_{hD}r_1) \right) \times \\
\times C_{j_{hD}+1,m_{hD}}^{j_{hD},m_{hD}} \left( \frac{2j_{cD}+1}{2j_{hD}+3} C_{l_1,0,j_{cD},0}^{j_{hD}+1,0} \times \\
\times C_{l_2,0,j_{cA},0}^{j_{hA}+1,0} C_{j_{hD}+1,m_{hD}}^{j_{hD},m_{hD}} \right) \times \\
\times \left( j_{j_{cA}}(k_{cA}r_2) \left( \sqrt{\frac{j_hA}{2j_{hA}+1}} j_{hA}+1(k_{hA}r_2) \right) \times \\
\times C_{j_{hA}+1,m_{hA}}^{j_{hA},m_{hA}} \left( \frac{2j_{cA}+1}{2j_{hA}+3} C_{l_2,0,j_{cA},0}^{j_{hA}+1,0} \times \\
\times C_{l_2,0,j_{cA},0}^{j_{hA}+1,0} C_{j_{hA}+1,m_{hA}}^{j_{hA},m_{hA}} \right) \times \\
\times \left( \sqrt{\frac{2j_{cA}+1}{2j_{hA}} + 1} \times \\
\times C_{l_2,0,j_{cA},0}^{j_{hA}+1,0} C_{l_2,0,j_{cA},m_{cA}}^{j_{hA}+1,m_{hA}} \right) \right) \times \\
\times i^{l_1-l_2}(2l_1+1)(2l_2+1) (I_0 - 2I_2),
\]

where \( I_0 \) and \( I_2 \) are represented by expressions (71). It can be shown that the selection rules for \( M^{(2)}_{\text{Coul}} \) are as follows

\[
\begin{align*}
\{ \quad & l_1 + l_2 = 0, \\
\{ & l_1 + l_2 - \text{odd}
\end{align*}
\]

(74)
In the case of \( l_1 + l_2 = 0 \), expression (73) is simplified to become

\[
M^{(2)}_{\text{coul}} = \frac{e^2}{\varepsilon d^3} \left( \frac{P}{E_g} \right)^2 A_c D A_{h2D} A_c A_{h2A} \int_0^{R_D} r_1^2 dr_1 \int_0^{R_A} r_2^2 dr_2 2\times \\
\times \left( j_{cD} (k_{cD} r_1) \left( \sqrt{\frac{j_{hD}}{2j_{hD} + 1}} j_{hD} (k_{hD} r_1) C_{j_{hD}+1,m_{hD}}^{j_{hD}+1,m_{hD}+1,0} \right. \right. \\
\times \delta_{j_{cD} j_{hD}+1} \delta_{m_{cD},m_{hD}} - \sqrt{\frac{j_{hD}}{2j_{hD} + 1}} j_{hD} (k_{hD} r_1) C_{j_{hD}-1,m_{hD},1,0}^{j_{hD}-1,m_{hD},1,0} \delta_{j_{cD} j_{hD}} \delta_{m_{cD},m_{hD}} \\
\times \left. \left. \left( j_{cA} (k_{cA} r_2) \left( \sqrt{\frac{j_{hA}}{2j_{hA} + 1}} j_{hA} (k_{hA} r_2) C_{j_{hA}+1,m_{hA},1,0}^{j_{hA}+1,m_{hA}+1,0} \delta_{j_{cA} j_{hA}+1} \delta_{m_{cA},m_{hA}} - \sqrt{\frac{j_{hA}}{2j_{hA} + 1}} j_{hA} (k_{hA} r_2) \right) \right. \right. \\
\times \left. \left. C_{j_{hA}-1,m_{hA},1,0}^{j_{hA}-1,m_{hA},1,0} \delta_{j_{cA} j_{hA}} \delta_{m_{cA},m_{hA}} \right) \right) \right),
\]

(75)

**Calculation of exchange interaction integrals**

The integrals in (45) are calculated for transitions between levels with full angular momenta \( j_{cD} = j_{cA} = 0 \) and \( j_{hD} = j_{hA} = 1 \). In the radial parts of wave functions (32), we pass to
cylindrical functions of half-integer order. Let us \( J_1 \) as \( J_1 = J_{11} + J_{12} + J_{13} \), where

\[
J_{11} = \sin(k_cD R_D) \exp(-\kappa_cD) \int_0^{R_A} \frac{1}{k_cD(d - z'_1)} \frac{\sin(k_cA z'_1)}{k_cA z'_1} \exp(\kappa_cD z'_1) d z'_1 \times
\]

\[
\times \{ \exp(-\kappa_hD(d - R_D)) \times
\]

\[
\times \left\{ \left( \frac{\sin(k_hD R_D)}{k_hD R_D} - \cos(k_hD R_D) \right) \exp(\kappa_hD z_2) P(\eta_2^2) d z_2 + \right. \]

\[
+ \left( \frac{\sin(k_hA R_A)}{k_hA R_A} - \cos(k_hA R_A) \right) \left( \frac{\sin(k_hA R_A)}{k_hA R_A} - \cos(k_hA R_A) \right) \exp(-\kappa_hD(d - R_D)) \exp(\kappa_hA R_A) + \right. \]

\[
+ \int_{R_A}^{d - R_D} \frac{1}{k_hD(d - z_2)} \frac{1}{k_hA z_2} \exp((\kappa_hD - \kappa_hA) z_2) P(\eta_2^2) d z_2 + \left. \left( \frac{\sin(k_hA R_A)}{k_hA R_A} - \cos(k_hA R_A) \right) \times \right. \]

\[
\times \exp(k_hA R_A) \int_{d - R_D}^{d} \frac{1}{k_hA z_2} \frac{1}{k_hD(d - z_2)} \left( \frac{\sin(k_hD (d - z_2))}{k_hD(d - z_2)} - \cos(k_hD(d - z_2)) \right) \exp(-\kappa_hA z_2) P(\eta_2^2) d z_2; \]

(76)
\[ J_{12} = \frac{1}{2\rho_{\max} k_A} \sin(k_c D) \exp(-\kappa_c D (d - R_D)) \times \]
\[ \times \int_{0}^{R_A} \frac{1}{k_c D (d - z_1')} \exp(\kappa_c D z_1') dz_1' \times \]
\[ \times \left\{ \left( \frac{\sin(k_h D R_D)}{k_h D R_D} - \cos(k_h D R_D) \right) \exp(-\kappa_h D (d - R_D)) \times \right. \]
\[ \times \left[ -2 \int_{0}^{z_1'} \frac{1}{k_h D (d - z_2)} \frac{1}{k_h A z_2} \times \right. \]
\[ \times \left( \frac{k_h A z_2}{k_h A z_2} - \cos(k_h A z_2) \right) \exp(k_h D z_2) dz_2 + \right. \]
\[ + \left. \int_{0}^{R_A} \frac{1}{k_h D (d - z_2)} \frac{1}{k_h A z_2} \left( \frac{\sin(k_h A z_2)}{k_h A z_2} - \cos(k_h A z_2) \right) \exp(k_h D z_2) dz_2 \right] + \]
\[ + \left( \frac{\sin(k_h D R_D)}{k_h D R_D} - \cos(k_h D R_D) \right) \left( \frac{\sin(k_h A R_A)}{k_h A R_A} - \cos(k_h A R_A) \right) + \]
\[ + \exp(-\kappa_h D (d - R_D) + k_h A R_A) \times \]
\[ \int_{d-R_D}^{d-R_D} \frac{1}{k_h D (d - z_2)} \frac{1}{k_h A z_2} \exp((\kappa_h D - k_h A) z_2) dz_2 + \]
\[ + \left( \frac{\sin(k_h A R_A)}{k_h A R_A} - \cos(k_h A R_A) \right) \exp(k_h A R_A) \times \]
\[ \times \int_{d-R_D}^{d-R_D} \frac{1}{k_h D (d - z_2)} \frac{1}{k_h A z_2} \times \]
\[ \times \left( \frac{\sin(k_h D (d - z_2))}{k_h D (d - z_2)} - \cos(k_h D (d - z_2)) \right) \exp(-k_h A z_2) dz_2 \right\} ; \]
\[ J_{13} = -\frac{1}{2\rho_{\text{max}} k_{cA}} \sin(k_{cD} R_D) \exp(-\kappa_{cD}(d - R_D)) \int_{0}^{R_A} \frac{1}{k_{cD}(d - z'_1)} \frac{1}{k_{cA} z'_1} \sin(k_{cA} z'_1) dz'_1 \times \]
\[ \times \left\{ \left( \frac{\sin(k_{hD} R_D)}{k_{hD} R_D} - \cos(k_{hD} R_D) \right) \exp(-\kappa_{hD}(d - R_D)) \times \right. \]
\[ \times \left[ \int_{0}^{z'_1} \frac{1}{k_{hD}(d - z_2)} \left( \frac{\sin(k_{hA} z_2)}{k_{hA} z_2} - \cos(k_{hA} z_2) \right) \exp(k_{hD} z_2) dz_2 + \right. \]
\[ + \left( \frac{\sin(k_{hD} R_D)}{k_{hD} R_D} - \cos(k_{hD} R_D) \right) \left( \frac{\sin(k_{hA} R_A)}{k_{hA} R_A} - \cos(k_{hA} R_A) \right) \exp(-\kappa_{hD}(d - R_D) + \kappa_{hA} R_A) \times \]
\[ \times \left. \int_{d-R_A}^{d} \frac{1}{k_{hD}(d - z_2)} \left( \frac{\sin(k_{hD}(d - z_2))}{k_{hD}(d - z_2)} - \cos(k_{hD}(d - z_2)) \right) \exp(-\kappa_{hA} z_2) dz_2 \right\} \]
(78)

To calculate these integrals, the integrands containing sine and cosine functions are approximated with polynomials so that the error in calculating the integrals does not exceed 3%.

Let us consider \( J_{12} \):

\[ J_{12} = \frac{1}{2\rho_{\text{max}} k_{cA}} \sin(k_{cD} R_D) \exp(-\kappa_{cD}(d - R_D)) \int_{0}^{R_A} \frac{1}{k_{cD}(d - z'_1)} \frac{1}{k_{cA} z'_1} \exp(\kappa_{cD} z'_1) dz'_1 \times \]
\[ \times \left\{ \left( \frac{\sin(k_{hD} R_D)}{k_{hD} R_D} - \cos(k_{hD} R_D) \right) \exp(-\kappa_{hD}(d - R_D)) \times \right. \]
\[ \times \left[ -2 \left. \int_{0}^{z'_1} \frac{1}{k_{hD}(d - z_2)} \frac{1}{k_{hA} z_2} \left( \frac{\sin(k_{hA} z_2)}{k_{hA} z_2} - \cos(k_{hA} z_2) \right) \exp(k_{hD} z_2) dz_2 + \right. \]
\[ + \left. \int_{0}^{R_A} \frac{1}{k_{hD}(d - z_2)} \frac{1}{k_{hA} z_2} \left( \frac{\sin(k_{hA} z_2)}{k_{hA} z_2} - \cos(k_{hA} z_2) \right) \exp(k_{hD} z_2) dz_2 \right] + \right. \]
\[ + \left( \frac{\sin(k_{hD} R_D)}{k_{hD} R_D} - \cos(k_{hD} R_D) \right) \left( \frac{\sin(k_{hA} R_A)}{k_{hA} R_A} - \cos(k_{hA} R_A) \right) \exp(-\kappa_{hD}(d - R_D) + \kappa_{hA} R_A) \times \]
\[ \times \left. \int_{d-R_A}^{d} \frac{1}{k_{hD}(d - z_2)} \frac{1}{k_{hA} z_2} \exp((\kappa_{hD} - \kappa_{hA}) z_2) dz_2 + \left( \frac{\sin(k_{hA} R_A)}{k_{hA} R_A} - \cos(k_{hA} R_A) \right) \exp(\kappa_{hA} R_A) \times \right. \]
\[ \times \left. \int_{d-R_A}^{d} \frac{1}{k_{hD}(d - z_2)} \frac{1}{k_{hA} z_2} \left( \frac{\sin(k_{hD}(d - z_2))}{k_{hD}(d - z_2)} - \cos(k_{hD}(d - z_2)) \right) \exp(-\kappa_{hA} z_2) dz_2 \right\} \right. \]
(79)
In the integrals enclosed in square brackets, we change variables: \( k_{kA}z_2 = y \). Then, the first of the integrals in square brackets is transformed to

\[
\int_0^{1/y(k_{kA}d)} \frac{1}{1-y(k_{kA}d)} \left( \frac{\sin y}{y} - \cos y \right) \exp(ay) \, dy
\]

where the designation \( a = k_{kD}/k_{kA} \) is introduced. The replacement in this integral of the function \( \frac{1}{1-y(k_{kA}d)} \left( \frac{\sin y}{y} - \cos y \right) \) with the polynomial \( \frac{3}{8}y \left( 1 + \frac{y}{k_{kD}d} - \left( \frac{y}{k_{kD}d} \right)^2 \right) \left( 1 - \frac{y}{k_{kD}R_A} \right) \) makes it possible to easily calculate the integral to obtain

\[
\frac{1}{k_{hA}k_{hD}d} \exp(k_{hD}z_1') \frac{3}{8} \frac{1}{a^2} \left\{ [k_{hD}z_1' - 1 + \exp(-k_{hD}z_1')] - \frac{\alpha_A}{a} [(k_{hD}z_1')^2 - 2(k_{hD}z_1') + 2 - 2\exp(-k_{hD}z_1')] - \frac{\beta_A}{a^2} [(k_{hD}z_1')^3 - 3(k_{hD}z_1')^2 + 6(k_{hD}z_1') - 6 + 6\exp(-k_{hD}z_1')] + \frac{\gamma_A}{a^3} [(k_{hD}z_1')^4 - 4(k_{hD}z_1')^3 + 12(k_{hD}z_1')^2 - 24(k_{hD}z_1') + 24 - 24\exp(-k_{hD}z_1')] \right\}.
\]

where \( \alpha_A = (1/(k_{hD}R_A)) - (1/(k_{hD}d)), \beta_A = (1/(k_{hD}d))(1/(k_{hD}R_A)) + (1/(k_{hD}d)), \gamma_A = (1/(k_{hD}d)^2)(1/(k_{hD}R_A)) \). The second integral in square brackets is calculated in a similar way:

\[
\frac{1}{k_{hA}k_{hD}d} \exp(k_{hD}R_A) \frac{3}{8} \frac{1}{a^2} \left\{ (k_{hD}R_A) - 1 - \frac{\alpha_A}{a} [(k_{hD}R_A)^2 - 2(k_{hD}R_A) + 2] - \frac{\beta_A}{a^2} [(k_{hD}R_A)^3 - 3(k_{hD}R_A)^2 + 6(k_{hD}R_A) - 6] + \frac{\gamma_A}{a^3} [(k_{hD}R_A)^4 - 4(k_{hD}R_A)^3 + 12(k_{hD}R_A)^2 - 24(k_{hD}R_A) + 24] \right\}.
\]

After the change of variables \( k_{cA}z_1' = y \), the integral

\[
\int_0^{R_A} \frac{1}{k_{cD}(d-z'_1)} \sin(k_{cA}z'_1) \exp(k_{cD}z'_1) \, dz'_1
\]

is brought to the form

\[
\frac{1}{k_{cD}d} \frac{1}{k_{cA}} k_{cA} R_A \int_0^{1/y(k_{cA}d)} \sin(y) \exp(by) \, dy
\]

where \( b = k_{cD}/k_{cA} \). In this case, the integrand \( \frac{\sin(y)}{1-y/k_{cA}d} \) is modeled by the expression \( y(1+y/k_{cD}d + y^2/(k_{cD}d))(1-y/\pi) \).
As a result, we have

\[
\int_0^{R_A} \frac{1}{k_{cD}(d - z_1')} \sin(k_{cA}z_1') \exp(k_{cD}z_1')dz_1' = \frac{1}{k_{cD}d k_{cA}} \exp(-k_{cD}R_A) \times \\
\times \frac{1}{b^2} \left\{ [(k_{cD}R_A - 1) + \exp(-k_{cD}R_A)] - \left( \frac{1}{\pi} - \frac{1}{k_{cA}d} \right) \times \\
\times \frac{1}{b} \left[ (k_{cD}R_A)^2 - 2(k_{cD}R_A) + 2 - 2 \exp(-k_{cD}R_A) \right] + \\
+ \left( 1 - \frac{1}{\pi} \right) \frac{1}{b^2} \left[ (k_{cD}R_A)^3 - 3(k_{cD}R_A)^2 + 6(k_{cD}R_A) - 6 + 6 \exp(-k_{cD}R_A) \right] - \\
- \frac{1}{\pi} \frac{1}{k_{cA}d b^2} \left[ (k_{cD}R_A)^4 - 4(k_{cD}R_A)^3 + 12(k_{cD}R_A)^2 - 24(k_{cD}R_A) + 24 - 24 \exp(-k_{cD}R_A) \right] \right\}
\]

(82)

Substitution of expression (78) into \( \int_0^{R_A} f(z_1')dz_1' \) (77), replacement of variables \( k_{cA}z_1' = y \), and use of the auxiliary function \( \left( \frac{k_{hA}R_A}{10} y^2 \left( 1 - \frac{y^2}{k_{hA}k_{cA}} \right) \right) \) makes it possible to calculate this integral and obtain

\[
\frac{1}{k_{cA}k_{cD}d k_{hA}k_{hD}d} \exp((k_{cD} + k_{hD})R_A) \times \\
\times \frac{k_{hA}R_A}{10} \frac{1}{b^3} \left\{ (p k_{cA}R_A)^2 - 2(p k_{cA}R_A) + 2 \right\} - \\
- \frac{1}{k_{hA}R_A} \frac{1}{b^2} \left[ (p k_{cA}R_A)^4 - 4(p k_{cA}R_A)^3 + 12(p k_{cA}R_A)^2 - 24(p k_{cA}R_A) + 24 \right] \right\},
\]

(83)

where \( p = (k_{cD} + k_{hD})/k_{cA} \) The integral over the region between the QDs, \( R_A \leftrightarrow d - R_D \), in (76) is easily calculated if we take into account that

\[
\kappa_{hA} \cong \kappa_{hD} : \int_{R_A}^{d-R_D} \frac{1}{k_{hD}(d - z_2)} \frac{1}{k_{hA}z_2} \exp((\kappa_{hD} - \kappa_{hA})z_2)dz_2 \cong \\
\cong \frac{1}{k_{hD}d k_{hA}} \int_{R_A}^{d-R_D} \left( \frac{1}{z_2} + \frac{1}{d - z_2} \right) = \frac{1}{k_{hD}d} \frac{1}{k_{hA}} \ln \left( \frac{(d - R_D)(d - R_A)}{R_A R_D} \right)
\]

(84)
Calculation of the integral over the donor region:

\[
\int_{d-R_D}^{d} \frac{1}{k_{hD}(d - z_2)} \frac{1}{k_{hA}z_2} \left( \frac{\sin(k_{hD}(d - z_2))}{k_{hD}(d - z_2)} - \cos(k_{hD}(d - z_2)) \right) \exp(-\kappa_{hA}z_2)dz_2. \tag{85}
\]

By the replacement of variables: \( k_{hD}(d - z_2) = y \) the integral is brought to the form

\[
\frac{1}{k_{hD}d} \frac{1}{k_{hA}} \exp(-\kappa_{hA}d) \int_{0}^{k_{hD}R_D} \frac{1}{1 - y/(k_{hD}d)} \frac{1}{y} \left( \frac{\sin(y)}{y} - \cos(y) \right) \exp(cy)dy
\]

\((c = \kappa_{hD}/\kappa_{hA}), \text{considered above. As a result, we come to expression } (79), \text{in which it is necessary to change in the literal designations the indexes } A \text{ for } D. \text{ Let us write the final expression for integral } (77):\]

\[
J_{12} = \frac{1}{2\rho_{max}k_{cA}} \sin(k_{cD}R_D) \frac{1}{k_{cD}d} \frac{1}{k_{cA}d} \frac{1}{k_{hA}} \exp(-\kappa_{cD} + \kappa_{hD})(d - R_D - R_A)) \times
\]

\[
\times \left\{ \frac{\sin(k_{hD}R_D)}{(k_{hD}R_D)} - \cos(k_{hD}R_D) \right\} (B'_A + B_A) + \right. \]

\[
+ \left. \left\{ \frac{\sin(k_{hA}R_A)}{(k_{hA}R_A)} - \cos(k_{hA}R_A) \right\} \frac{\sin(k_{hA}R_A)}{(k_{hA}R_A)} - \cos(k_{hA}R_A) \right\} B_{A-D} + \right.
\]

\[
+ \left. \left\{ \frac{\sin(k_{hA}R_A)}{(k_{hA}R_A)} - \cos(k_{hA}R_A) \right\} B_{D} \right\} \tag{86}
\]

where

\[
B'_A = -2 \left( \frac{2}{k_{hD}R_A} \frac{1}{a^2} \right) \left( \frac{3}{4} \frac{1}{\gamma^2} \right) \left\{ 3(\gamma k_{cA}R_A - 1) - \frac{1}{\gamma} \left[ (\gamma k_{cA}R_A)^2 - 2(\gamma k_{cA}R_A) + 2 \right] \right\}. \tag{87}
\]
Here $a = \kappa_{hD}/k_{hA}$, $\gamma = (\kappa_{cD} + \kappa_{hD})/k_{cA}$;

\[
B_A = \left( \frac{2}{\kappa_{hD} R_A a^2} \right) \left\{ (\kappa_{hD} R_A)^2 - 2(\kappa_{hD} R_A) + 2 \right\} \times \\
\times \left( \frac{1}{b^2} \right) \left\{ [(\kappa_{cD} R_A - 1) + \exp(-\kappa_{cD} R_A)] - \left( \frac{1}{\pi} - \frac{1}{k_{cD} d} \right) \frac{1}{b} \left[ (\kappa_{cD} R_A)^2 - 2(\kappa_{cD} R_A) + 2 - 2(\kappa_{cD} R_A) \right] + \\
+ \left( 1 - \frac{1}{\pi} \right) \frac{1}{k_{cD} d} \frac{1}{b^2} \left[ (\kappa_{cD} R_A)^3 - 3(\kappa_{cD} R_A)^2 + 6(\kappa_{cD} R_A) - 6 + 6 \exp(-\kappa_{cD} R_A) \right] - \\
- \frac{1}{\pi} \frac{1}{k_{cD} d} \frac{1}{b^3} \left[ (\kappa_{cD} R_A)^4 - 4(\kappa_{cD} R_A)^3 + 12(\kappa_{cD} R_A)^2 - 24(\kappa_{cD} R_A) + 24 - 24 \exp(-\kappa_{cD} R_A) \right] \right\},
\]

where $b = \kappa_{cD}/k_{cA}$.

\[
B_{A-D} = \left( \frac{1}{b^2} \right) \left\{ [(\kappa_{cD} R_A) - 1 + \exp(-\kappa_{cD} R_A)] - \left( \frac{1}{\pi} - \frac{1}{k_{cD} d} \right) \times \\
\times \frac{1}{b} \left[ (\kappa_{cD} R_A)^2 - 2(\kappa_{cD} R_A) + 2 - 2 \exp(-\kappa_{cD} R_A) \right] + \\
+ \left( 1 - \frac{1}{\pi} \right) \frac{1}{b^2} \left[ (\kappa_{cD} R_A)^3 - 3(\kappa_{cD} R_A)^2 + 6(\kappa_{cD} R_A) - 6 + 6 \exp(-\kappa_{cD} R_A) \right] - \\
- \frac{1}{\pi} \frac{1}{k_{cD} d} \frac{1}{b^3} \left[ (\kappa_{cD} R_A)^4 - 4(\kappa_{cD} R_A)^3 + 12(\kappa_{cD} R_A)^2 - 24(\kappa_{cD} R_A) + 24 - 24 \exp(-\kappa_{cD} R_A) \right] \times \right\} \times \\
\times \ln \frac{(d - R_A)(d - R_D)}{R_AR_D}.
\]

In this expression, account is taken of the fact that $\kappa_{hA} \approx \kappa_{hD}$.

\[
B_{A-D} = \left( \frac{1}{b^2} \right) \times \left\{ [(\kappa_{cD} R_A) - 1 + \exp(-\kappa_{cD} R_A)] - \left( \frac{1}{\pi} - \frac{1}{k_{cD} d} \right) \times \\
\times \frac{1}{b} \left[ (\kappa_{cD} R_A)^2 - 2(\kappa_{cD} R_A) + 2 - 2 \exp(-\kappa_{cD} R_A) \right] + \\
+ \left( 1 - \frac{1}{\pi} \right) \frac{1}{b^2} \left[ (\kappa_{cD} R_A)^3 - 3(\kappa_{cD} R_A)^2 + 6(\kappa_{cD} R_A) - 6 + 6 \exp(-\kappa_{cD} R_A) \right] - \\
- \frac{1}{\pi} \frac{1}{k_{cD} d} \frac{1}{b^3} \left[ (\kappa_{cD} R_A)^4 - 4(\kappa_{cD} R_A)^3 + 12(\kappa_{cD} R_A)^2 - 24(\kappa_{cD} R_A) + 24 - 24 \exp(-\kappa_{cD} R_A) \right] + \\
+ 24 - 24 \exp(-\kappa_{cD} R_A) \right\} \times \left( \frac{2}{k_{hD} R_D c^2} \right) \left\{ (\kappa_{cD} R_A) - 1 - \frac{1}{(\kappa_{cD} R_A)} \times \\
\times \left[ (\kappa_{cD} R_A)^2 - 2(\kappa_{cD} R_A) + 2 \right] \right\},
\]

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here $c = \kappa_{hD}/\kappa_{hA}$. The integrals appearing in $J_2, J_3$ are calculated in a similar manner. The substitution of the system parameter numerical values in the obtained expressions results in (46). Two recent papers\textsuperscript{62,63} support our result that in the systems including QDs the exchange interaction can play a significant role in the energy transfer at small donor-acceptor separation. It is experimentally shown in\textsuperscript{62} that in the CdSe QD-Squaraine light harvesting assemblies, the exchange (Dexter) process is essential to the energy transfer and dominates the dipole-based Forster one at the smaller QDs. In\textsuperscript{63} the measured energy transfer rates in the close-packed blends of CdSe/CdZnS core/shell QDs are found to be more than an order of magnitude larger than the rate predicted by Forster theory, which cannot be satisfactory explained by several possible factors considered in the paper. We believe that exchange contribution to the energy transfer should be also taken into account for the consideration the discrepancy.

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