ЖЭТФ, 2016, том 149, вып. 3, стр. 614–622

NONRADIATIVE AND RADIATIVE FÖRSTER ENERGY TRANSFER BETWEEN QUANTUM DOTS

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Received November 10, 2015

We theoretically study nonradiative and radiative energy transfer between two localized quantum emitters, a donor (initially excited) and an acceptor (receiving the excitation). The rates of nonradiative and radiative processes are calculated depending on the spatial and spectral separation between the donor and acceptor states and for different donor and acceptor lifetimes for typical parameters of semiconductor quantum dots. We find that the donor lifetime can be significantly modified only due to the nonradiative Förster energy transfer process at donor–acceptor separations of approximately 10 nm (depending on the acceptor radiative lifetime) and for the energy detuning not larger than 1–2 meV. The efficiency of the nonradiative Förster energy transfer process under these conditions is close to unity and decreases rapidly with an increase in the donor–acceptor distance or energy detuning. At large donor–acceptor separations greater than 40 nm, the radiative corrections to the donor lifetime are comparable with nonradiative ones but are relatively weak.

Contribution for the JETP special issue in honor of L. V. Keldysh's 85th birthday

DOI: 10.7868/S0044451016030135

1. INTRODUCTION

Förster energy transfer (ET) processes are now actively studied in various fields that bridge physics, biology, and chemistry. The energy is transferred from the initially excited (donor) system to the system that is initially unexcited (acceptor) via the electromagnetic interaction [1]. This is an incoherent one-way transfer followed by the rapid emission or nonradiative recombination from the acceptor state, which must be distinguished from coherent light-induced coupling [2]. In what follows, we use the terms "donor" and "acceptor" for the energy transmitting and receiving systems. Although these terms are quite established in the literature on Förster processes, they are somewhat ambiguous and should not be confused with donor and acceptor impurities in a semiconductor. Here, they characterize excitation transfer and not the charge transfer. The donor and acceptor systems can be realized as quantum dots [3–6], quantum wires [7], quantum wells [8, 9] and colloidal nanoplatelets [10], biological molecules [11, 12], and defects in a semiconductor [13, 14]. Typically, the range of the Förster interaction is of the order of several nm [15]. By placing the donors and acceptors into the structured electromagnetic environment, one can try to enhance the efficiency of the transfer. In particular, the transfer mediated by localized and surface plasmons [16, 17], photons trapped in a cavity [18] or localized in random glass [12], as well as modified by metamaterials [19, 20] is now actively studied. The concept of tailored photon-induced energy transfer shares many features with the Purcell enhancement [21] of spontaneous emission in a cavity as compared to that in the vacuum. Indeed, in the first case, we can think of nonradiative energy transfer from the donor to the acceptor via (virtual) photons, while in the second case, the energy is radiated into the real photonic modes (see Fig. 1). A general theory of the Förster transfer process has been developed in detail [22–27]. However, the relation between transfer processes and the Purcell effect as well as the character of the transfer in each particular nanosystem, radiative or nonradiative, remains a subject of active discussions [17, 19, 28, 29]. Simultaneous enhancement and control of the energy transfer and spontaneous emission processes in the same electromagnetic environment are quite challenging.

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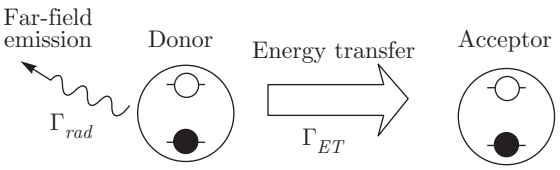

Fig. 1. Schematic illustration of the energy transfer and photon radiation processes

Here, we study the simplest case of localized donor and acceptor (e. g., quantum dots) embedded in a dielectric matrix. We first revisit different approaches to calculating the rate of the transfer process and obtain it consistently with the donor spontaneous decay rate (Sec. 2). Next, we discuss the transfer kinetics (Sec. 3) and analyze the radiative and nonradiative contributions to the Förster process depending on the spatial and spectral separation of the donor and the acceptor as well as their intrinsic radiative lifetime (Sec. 4).

2. CALCULATION OF THE TRANSFER RATES

We consider the energy transfer between two emitters in an unbounded dielectric matrix with a permittivity ε, located at points $\mathbf{r}_D$ (donor) and $\mathbf{r}_A = \mathbf{r}_D + \mathbf{r}$ (acceptor). The relevant donor and acceptor states are characterized by the energies $E_D = \hbar\omega_D$ and $E_A = \hbar\omega_A$ and the transition dipole matrix elements $\mathbf{d}_D$ and $\mathbf{d}_A$. In what follows, we neglect the dispersion and losses in the matrix. We first present the Fermi Golden rule result for the transfer rate (Sec. 2.1) and then compare it with the semiclassical Langevin approach (Sec. 2.2).

2.1. Fermi Golden rule

The Fermi Golden rule yields the following expression for the transfer rate:

$$\Gamma_{ET,0} = \frac{2\pi}{\hbar}\delta(E_D - E_A)|\mathbf{d}_D\hat{G}_0\mathbf{d}_A|^2\,, \qquad (1)$$

where

$$G_{0,\alpha\beta} = \frac{3r_\alpha r_\beta - r^2\delta_{\alpha\beta}}{\varepsilon r^5} \qquad (2)$$

is the electromagnetic Green's function evaluated in the electrostatic approximation and describing the dipole–dipole coupling between the donor and the acceptor [15]. This result can be applied for quantum dots as well as molecules. For quantum dots, we have neglected the local field corrections for the electric field [30, 31], assuming the permittivities of the dot and the matrix to be the same. In the case of spherical dots, these corrections lead to a renormalization of the dipole matrix element, $\mathbf{d}_{D,A} \to \mathbf{d}_{D,A}3\varepsilon_{QD}/(\varepsilon_{QD} + 2\varepsilon)$, where ε_{QD} is the dot permittivity. In the general case, we have to introduce the depolarization factors depending on the dot orientation and shape. Additional local field corrections appear for dense arrays of quantum dots [31, 32].

The result in Eq. (1) scales with the distance as $1/r^6$. However, Eq. (1) neglects any effects of retardation for the electromagnetic interaction. When the retardation effects are taken into account, the transfer rate can still be represented in form (1), but the electrostatic potential in Eq. (2) should be replaced by the full retarded electromagnetic Green's tensor [24]

$$G_{\alpha\beta} = \left(\delta_{\alpha\beta} + \frac{1}{q^2}\frac{\partial^2}{\partial x_\alpha \partial x_\beta}\right)\frac{e^{iqr}}{\varepsilon r} \qquad (3)$$

evaluated at the transition frequency $\omega = E_D/\hbar \equiv E_A/\hbar$, where $q = \omega_D\sqrt{\varepsilon}/c$, such that

$$\Gamma_{ET} = \frac{2\pi}{\hbar}\delta(E_D - E_A)|\mathbf{d}_D\hat{G}\mathbf{d}_A|^2\,. \qquad (4)$$

In this case, the long-range radiative transfer, which scales with the distance as $1/r^2$, becomes possible [15]. The explicit values for the matrix elements of the interaction $g = \mathbf{d}_D\hat{G}_0\mathbf{d}_A$ in the cases where the dipole momenta of the donor and the acceptor are parallel to each other and either parallel or perpendicular to the vector $\mathbf{r} = \mathbf{r}_D - \mathbf{r}_A$ are given by

$$\begin{aligned} g_\parallel &= d_A d_D \frac{e^{iqr}}{\varepsilon}\left(\frac{2}{r^3} - \frac{2iq}{r^2}\right), \\ g_\perp &= d_A d_D \frac{e^{iqr}}{\varepsilon}\left(-\frac{1}{r^3} + \frac{iq}{r^2} + \frac{q^2}{r}\right). \end{aligned} \qquad (5)$$

For a random mutual orientation of the donor and acceptor matrix elements, the transfer is described by the value $|g^2| = (1/3)|g_\parallel^2| + (2/3)|g_\perp^2|$, averaged over the orientations.

2.2. Semiclassical approach

Here, we re-derive Eq. (1) within the Langevin random source technique and the semiclassical theory of light–matter interaction [33–35].

1. Radiative decay of the donor

We start with the radiative decay of the donor state in the absence of acceptors. The donor electric polarizability tensor is given by

$$\alpha_{\mu\nu}(E) = \frac{d_{D,\mu}d_{D,\nu}}{E_D - E}. \qquad (6)$$

Its dipole moment $\mathbf{p}_D$ induced by the external electric field $\mathbf{E}$ at the frequency $\hbar\omega$ is given by

$$\mathbf{p}_D = \frac{\mathbf{d}_D\big[\mathbf{d}_D \cdot \mathbf{E}(\mathbf{r}_D)\big]}{E_D - \hbar\omega}\,. \tag{7}$$

On the other hand, the electric field of the donor is determined by the Green's function in Eq. (3),

$$\mathbf{E}(\mathbf{r}) = \hat{G}(\mathbf{r} - \mathbf{r}_D)\mathbf{p}_D\,. \tag{8}$$

Combining Eq. (7) and Eq. (8), we obtain the self-consistency condition for the mode of the donor coupled to its own electromagnetic field:

$$(E_D - \hbar\omega)\mathbf{p}_D = \mathbf{d}_D[\mathbf{d}_D \cdot \hat{G}(0,\omega)\mathbf{p}_D]\,. \tag{9}$$

This equation allows determining the modification of the lifetime of the donor state due to interaction with light. The energy shift of the donor state can be obtained as well, but this requires regularizing the Green's function taking the finite extent of the wave function into account (see Refs. [30, 33]). Below, we assume that such a regularization has already been performed and is included in the definition of the energy E_D. We also use the weak-coupling approximation, with the Green function in the right-hand side of Eq. (9) evaluated at the frequency ω_D. The spontaneous emission rate is then determined from Eq. (9) as

$$\Gamma_{rad,0} \equiv -2\,\mathrm{Im}\,\omega = 2d_{D,\alpha}\,\mathrm{Im}\,\hat{G}_{\alpha\beta}(0,\omega_D)d_{D,\beta}, \tag{10}$$

or, explicitly [36],

$$\Gamma_{rad,0} = \frac{4d_D^2}{3\hbar}\left(\frac{\omega_D}{c}\right)^3\sqrt{\varepsilon}\,. \tag{11}$$

2. Donor decay in the presence of an acceptor

Equation (11) is a textbook result for the spontaneous emission rate [36]. However, the approach above can be straightforwardly generalized to include energy transfer processes [37, 38]. For this, Eqs. (8), (9) should be modified to account for the electromagnetic coupling of the donor and the acceptor as follows:

$$\begin{aligned}&(\omega_D - \omega)\mathbf{p}_D = \\ &= \frac{1}{\hbar}\mathbf{d}_D[\mathbf{d}_D \cdot (\hat{G}(0,\omega)\mathbf{p}_D) + \hat{G}(\mathbf{r},\omega)\mathbf{p}_A],\\ &(\omega_A - i\gamma_A - \omega)\mathbf{p}_A = \frac{1}{\hbar}\mathbf{d}_A[\mathbf{d}_A \cdot \hat{G}(\mathbf{r},\omega)\mathbf{p}_D].\end{aligned} \tag{12}$$

Here, we include the phenomenological (nonradiative) decay rate γ_A for the acceptor excited state. The decay is due to the energy relaxation to the lower acceptor states. We are interested in the weak-coupling regime, and consider the energy relaxation of the acceptor state to be much faster than the energy transfer and the radiative decay of both donor and acceptor states. Hence, the donor lifetime in the presence of the acceptor is given by the perturbative solution of system (12) at a frequency close to ω_D. The result can be represented as

$$\frac{1}{\tau_{D,0}} = \Gamma_{rad,0}\,, \quad \frac{1}{\tau_D} = \Gamma_{rad,0} + \Gamma_D, \tag{13}$$

$$\begin{aligned}\Gamma_D = &\frac{2}{\hbar}\times\\ &\times\,\mathrm{Im}\left[\frac{1}{\omega_A - i\gamma_A - \omega_D}\,\frac{1}{\hbar^2}\left(\mathbf{d}_D \cdot \hat{G}(\mathbf{r})\,\mathbf{d}_A\right)^2\right].\end{aligned} \tag{14}$$

The second term in Eq. (13) describes the acceptor-induced contribution to the decay rate of the donor state. This expression is quite different from the standard result in Eq. (4). First, Eq. (14) includes a finite lifetime of the acceptor state. Second, the functional dependence of Eq. (4) and Eq. (14) on the (complex) Green's function is different. The difference between Eq. (4) and Eq. (14) constitutes the central result in this paper. Qualitatively, it occurs because Eq. (4) describes only the rate of the generation of particles in the acceptor state. On the other hand, Eq. (14) is the total acceptor-induced modification of the donor decay rate, to which both the energy transfer to the acceptor and the modification of the spontaneous decay rate contribute. In Sec. 4 below, we analyze Eq. (4) and Eq. (14) in more detail. Here, we only mention that in the case where the distance between the donor and the acceptor becomes much smaller than the wavelength, $qr \ll 1$, and the retardation effects are neglected, Eq. (14) reduces to

$$\Gamma_{D,0} = \frac{2\pi}{\hbar}\,\frac{1}{\pi\hbar}\,\frac{\gamma_A}{(\omega_D - \omega_A)^2 + \gamma_A^2}\,|\mathbf{d}_D\hat{G}_0\mathbf{d}_A|^2. \tag{15}$$

This expression is equivalent to the Fermi Golden rule result in Eq. (1) in the limit of the vanishing acceptor decay rate. Here, we consider only the case of a transparent medium, $\mathrm{Im}\,\varepsilon = 0$. The more general case of a lossy medium, where the additional decay channel due to medium heating is possible, has been analyzed in Ref. [39] (see also Ref. [40]).

3. Population of acceptors

In the preceding paragraph, we have calculated the decay rates of donor state. Now we obtain the acceptor population using the same semiclassical technique. For this, we consider the regime of stationary incoher-

ent pumping and use the random source approach [35]. Hence, system (12) is modified as

$$\begin{aligned}(\omega_D-\omega)\mathbf{p}_D &= \frac{1}{\hbar}\mathbf{d}_D[\mathbf{d}_D\cdot(\hat{G}(0,\omega)\mathbf{p}_D)+\\ &+\hat{G}(\mathbf{r},\omega)\mathbf{p}_A]+\mathbf{d}_D\xi(\omega),\\ (\omega_A-i\gamma_A-\omega)\mathbf{p}_A &= \frac{1}{\hbar}\mathbf{d}_A[\mathbf{d}_A\cdot\hat{G}(\mathbf{r},\omega)\mathbf{p}_D],\end{aligned} \tag{16}$$

where $\xi(\omega)$ is a random source term describing the stationary incoherent generation of excitons in the donor state. Generally, the correlations of random sources are determined by the pumping mechanism [41], the simplest approximation corresponding to white Gaussian noise

$$\begin{aligned}\langle\xi^*(\omega)\xi(\omega')\rangle &= \frac{S}{2\pi}\delta(\omega-\omega'),\\ \langle\xi^*(t)\xi(t')\rangle &= S\delta(t-t'),\end{aligned} \tag{17}$$

where S is the exciton generation rate. We first calculate the stationary donor state population as

$$N_D = \frac{\langle|\mathbf{p}_D(t)|^2\rangle}{|\mathbf{d}_D|^2}, \tag{18}$$

where

$$\mathbf{p}_D(t) = \int\frac{d\omega}{2\pi}\mathbf{p}_D(\omega)e^{-i\omega t} \tag{19}$$

and the angular brackets denote averaging over the random source realizations. Explicitly, we obtain

$$N_D = \left\langle\left|\int\frac{d\omega}{2\pi}\mathcal{D}_D(\omega)\xi(\omega)e^{-i\omega t}\right|^2\right\rangle, \tag{20}$$

where

$$\mathcal{D}_D(\omega) = \frac{1}{\omega_D-\omega-i/(2\tau_D)} \tag{21}$$

is the donor Green's function calculated including both the energy transfer and radiative decay processes. Averaging and integrating yields $N_D = S\tau_D$, i. e., the donor population equal to the lifetime times the generation rate. The acceptor population is obtained in a similar way as

$$\begin{aligned}N_A \equiv \frac{\langle|\mathbf{p}_A|^2\rangle}{|\mathbf{d}_A|^2} &= S|\mathbf{d}_D\cdot\hat{G}_0\mathbf{d}_A|^2\times\\ &\times\int\frac{d\omega}{2\pi}|\mathcal{D}_A(\omega)|^2|\mathcal{D}_D(\omega)|^2\end{aligned} \tag{22}$$

with

$$\mathcal{D}_A(\omega) = \frac{1}{\omega_A-\omega-i\gamma_A}\,. \tag{23}$$

The result of integration is

$$\begin{aligned}N_A = \frac{2\pi}{\hbar}S\tau_D\tau_A\frac{1}{\pi\hbar}\,&\frac{\gamma_A}{(\omega_A-\omega_D)^2+\gamma_A^2}\times\\ &\times|\mathbf{d}_D\hat{G}_0\mathbf{d}_A|^2\,,\end{aligned} \tag{24}$$

where $\tau_A = 1/(2\gamma_A)$. It is instructive to rewrite this result in the form of a kinetic equation for balance of the (nonradiative) decay in the acceptor state and the energy transfer from the donors:

$$\frac{N_A}{\tau_A} = \Gamma_{ET}N_D\,. \tag{25}$$

Using this equation as the definition of the energy transfer rate Γ_{ET}, we find from Eq. (24) that

$$\begin{aligned}\Gamma_{ET} &= \frac{2\pi}{\hbar}\Theta|\mathbf{d}_D\cdot\hat{G}\mathbf{d}_A|^2,\\ \Theta &= \frac{1}{\pi\hbar}\,\frac{\gamma_A}{(\omega_A-\omega_D)^2+\gamma_A^2},\end{aligned} \tag{26}$$

which is the generalization of Eq. (4) to the case of a finite acceptor state lifetime. Equation (26) directly corresponds to the expression commonly used for realistic multilevel systems [3, 5] (e. g., Eq. (1) in Ref. [5]) with Θ being the overlap integral between the donor emission and the acceptor absorption spectra for the considered model with the two-level donor and acceptor. We note that these results can be equivalently obtained using the Keldysh diagram technique [42]; its correspondence to the Langevin source technique for this problem is discussed in Refs. [35, 41].

2.3. Ohmic losses approach

The acceptor excitation rate in Eq. (26) can also be calculated in a slightly different but equivalent way as the rate of the absorption of donor emission [8, 16]. This allows interpreting the energy transfer process in the form of Ohmic losses for the donor emission. Thus, we can separate the contributions to the total donor decay rate (14) into those determined by the energy transfer process and by the modification of the far-field emission by the acceptor.

In particular, the acceptor dipole moment induced by the donor with the dipole moment $\mathbf{p}_D = \mathbf{d}_D$ is obtained from the second equation in (12) as

$$p_{A,\alpha} = \frac{d_{A,\alpha}d_{A,\beta}G_{\beta\gamma}d_{D,\gamma}}{\hbar(\omega_A-\omega_D-i\gamma_A)}\,, \tag{27}$$

and the electric field at the acceptor position is given by

$$E_\alpha(\mathbf{r}_A) = G_{\alpha\beta'}(\mathbf{r})\,d_{D,\beta'}\,. \tag{28}$$

The rate of power absorption is then determined by the standard electrodynamic expression [43]

$$\frac{1}{\tau_{ET}} \equiv \Gamma_{ET} = 2\,\mathrm{Im}\,p_{A,\alpha}E^*_{D,\alpha}. \tag{29}$$

Substituting Eqs. (27) and (28) in Eq. (29), we recover Eq. (26).

To distinguish between the energy transfer and the far-field emission processes, we use the identity [34]

$$\int d^3r'' G_{\mu\nu}(\mathbf{r},\mathbf{r}'')G^*_{\mu'\nu}(\mathbf{r}',\mathbf{r}'')\varepsilon''(\mathbf{r}'') = \\ = 4\pi \operatorname{Im} G_{\mu\mu'}(\mathbf{r},\mathbf{r}') \quad (30)$$

valid for the Green's function in an arbitrary medium in the case of a zero external stationary magnetic field. For $\mathbf{r}=\mathbf{r}'$, the right-hand side determines the local density of photonic states and the radiative decay rate [44]. For $\mu=\nu'$ and $\mathbf{r}=\mathbf{r}'$, Eq. (30) is simplified to

$$\operatorname{Im}\int d^3r'' \frac{\varepsilon(\mathbf{r}'')-1}{4\pi}|G^*_{\mu'\nu}(\mathbf{r}'',\mathbf{r})|^2 = \\ = \operatorname{Im} G_{\mu\mu}(\mathbf{r},\mathbf{r})\,. \quad (31)$$

The radiative decay rate is due to the far-field emission and due to the Joule heating of the medium. The Joule losses are determined as the integral in the left-hand side over the finite volume where $\operatorname{Im}\varepsilon \neq 0$. The far-field emission is given from the contribution to the integral at $r''\to\infty$ for $\operatorname{Im}\varepsilon(\mathbf{r}'')\to 0$. For a given μ, the integral can be rewritten as $\operatorname{Im}\int d^3r''\mathbf{\Pi}(\mathbf{r}'')\mathbf{E}^*(\mathbf{r}'')$, where Π is the polarizability tensor,

$$\Pi_\beta(\mathbf{r}'') = \frac{\varepsilon(\mathbf{r}'')-1}{4\pi}G_{\beta\alpha}(\mathbf{r}'',\mathbf{r}), \\ E_\beta(\mathbf{r}'') = G_{\beta\alpha}(\mathbf{r}'',\mathbf{r})\,. \quad (32)$$

This expression is equivalent to Eq. (29) and corresponds to the transfer rate Γ_{ET} in Eq. (26). The total acceptor-induced decay rate of the donor state Γ_D in Eq. (14) includes contribution (26) due to the Ohmic losses and a correction to the far-field emission. Thus, the far-field contribution is obtained as the difference between Γ_D and Γ_{ET},

$$\Delta\Gamma_{rad} = \Gamma_D - \Gamma_{ET}\,. \quad (33)$$

3. KINETIC EQUATIONS

In the preceding section, we have presented four approaches yielding consistent results, namely (i) the Fermi Golden rule to calculate the transfer rate to the acceptor state, Eq. (1), neglecting the losses and retardation, (ii) the coupled-dipole technique to calculate the donor decay rate, Eq. (14), (iii) the random sources technique, and (iv) the Joule power losses approach to calculate the transfer rate for the acceptor state, Eq. (26).

These results allow us to formulate the following system of phenomenological kinetic equations for the population of the donor and acceptor states N_D and N_A, and the population $N_{A,0}$ of the acceptor ground (emitting) state whose lifetime $\tau_{A,0}$ is controlled by spontaneous emission:

$$\frac{dN_D}{dt} = -\left(\Gamma_{rad,0}+\Delta\Gamma_{rad}\right)N_D - \Gamma_{ET}N_D + S \equiv \\ \equiv -\frac{N_D}{\tau_D} + S\,, \\ \frac{dN_A}{dt} = -\frac{N_A}{\tau_A} + \Gamma_{ET}N_D\,, \\ \frac{dN_{A,0}}{dt} = -\frac{N_{A,0}}{\tau_{A,0}} + \frac{N_A}{\tau_A}\,. \quad (34)$$

Here, S is the exciton generation rate for the donor state, and the total acceptor-induced correction to the donor decay rate $\Gamma_D = \Gamma_{ET} + \Delta\Gamma_{rad}$ consists of two parts, the correction due to acceptor excitation (Γ_{ET}) and the correction corresponding to the far-field emission ($\Delta\Gamma_{rad}$). In the case of a short distance between the donor and the acceptor, the value of g is almost real, $\Gamma_D = \Gamma_A$ and $\Gamma_{rad} \ll \Gamma_D$. The expression for Γ_{rad} can be explicitly written as

$$\Delta\Gamma_{rad} = -\frac{4}{\hbar}\,\frac{2(\operatorname{Im} g)^2\gamma_A + 2\Delta\operatorname{Im}(g)\operatorname{Re} g}{\Delta^2+\gamma_A^2}\,, \quad (35)$$

where $g = \mathbf{d}_D\cdot\hat{G}\mathbf{d}_A$ and $\Delta = \omega_D - \omega_A$. Hence, $\Delta\Gamma_{rad}$ is not equal to zero only when the retardation effects are taken into account ($\operatorname{Im} g \neq 0$). This means that the term $\Delta\Gamma_{rad}$ corresponds to the radiation of real photons. On the other hand, Γ_{ET} is proportional to $(\operatorname{Re} g)^2 + (\operatorname{Im} g)^2$, i. e., it includes contributions of both real and virtual photons [25].

In the general case, the values of $\Delta\Gamma_{rad}$ and Γ_D can be negative. For the vanishing detuning between the donor and the acceptor ($\Delta = 0$), we have $|\Gamma_D| < \Gamma_{ET}$, and $\Delta\Gamma_{rad} < 0$ and hence the far-field emission is suppressed (see Eq. (35)). For a large detuning ($|\Delta| \gg \gg \gamma_A$), the value of Γ_{rad} can be positive, i. e., the far field emission enhanced. It is also possible that Γ_D is equal to zero, but Γ_{ET} is not zero. This means that the growth of the donor decay rate due to the transfer is exactly compensated by the suppression of the far-field emission from the donor.

We stress that the lifetime of the acceptor excited state τ_A is determined in our model by the nonradiative process and is the shortest time in the system, while the lifetime of the acceptor ground state $\tau_{A,0}$ is of the same order as $\tau_{D,0}$, such that $\tau_A \ll \tau_{A,0} \approx \tau_{D,0}$. As discussed above, the donor lifetime τ_D can be de-

creased or increased in the presence of an acceptor, but the condition $\tau_A \ll \tau_D$ remains valid.

The dynamics of the system Eq. (24) in the absence of stationary pumping for a given population of donors at $t = 0$ under these conditions is given by

$$\begin{aligned} N_D &= N_D(0)\,\exp\left(-\frac{t}{\tau_D}\right), \\ N_A &= \Gamma_{ET} N_D(0) \frac{\tau_A \tau_D}{\tau_A - \tau_D} \times \\ &\times \left(\exp\left(-\frac{t}{\tau_A}\right) - \exp\left(-\frac{t}{\tau_D}\right)\right) \approx \\ &\approx \Gamma_{ET} N_D(0) \tau_A \exp\left(-\frac{t}{\tau_D}\right), \\ N_{A,0} &= \Gamma_{ET} N_D(0) \frac{\tau_{A,0} \tau_D}{\tau_{A,0} - \tau_D} \times \\ &\times \left(\exp\left(-\frac{t}{\tau_{A,0}}\right) - \exp\left(-\frac{t}{\tau_D}\right)\right). \end{aligned} \tag{36}$$

For stationary pumping, the solution of Eqs. (24) is given by

$$N_D = G\tau_D, \quad N_A = \Gamma_{ET}\tau_A N_D, \quad N_{A,0} = \Gamma_{ET}\tau_{A,0} N_D. \tag{37}$$

The acceptor population in the ground (emitting) state can also be rewritten as

$$N_{A,0} = G\tau_{A,0} K_{ET}\,, \tag{38}$$

where

$$K_{ET} = \frac{\Gamma_{ET}}{1/\tau_{D,0} + \Gamma_D} = \frac{\Gamma_{ET}\tau_{D,0}}{1 + \Gamma_D \tau_{D,0}} \tag{39}$$

is the efficiency of the energy transfer. If we assume that the quantum yield of donor emission without an acceptor is equal to unity and its intensity is just given by $I_D = G$, the modified donor intensity in the presence of the acceptor is given by $I_D^* = G(1 - K_{ET})$, while the intensity from the acceptor is $I_A^* = GK_{ET}$. It turns out that in the presence of FRET with $\Gamma_{ET} > 0$, the quantum efficiency of the donor PL is always decreased even in the case $\Delta\Gamma_{rad} > 0$ (increase in the donor radiative rate). However, the increase in the donor radiative rate decreases the efficiency of the energy transfer and vice versa, without changing the energy transfer rate Γ_{ET}.

4. RESULTS AND DISCUSSION

We now proceed to the analysis of the transfer efficiency and transfer rates. We study their dependence on the donor–acceptor distance r (Fig. 2), radiative lifetimes $\tau_{rad,0}$ (Fig. 3), and the spectral detunings Δ (Fig. 4). Figure 2 examines the distance dependence of the efficiency K_{ET} (*a*,*b*) and the rates Γ_{ET}, Γ_D, Γ_{rad}, and $\Gamma_D + \Gamma_{rad,0}$ (*c*,*d*). We have chosen two respresentative values of the dipole matrix elements $d_D = d_A$, resulting in the bare radiative lifetimes $\tau_{rad,0} = 1$ ns (Fig. 2*a* and 2*c*) and $\tau_{rad,0} = 100$ ns (Fig. 2*b* and 2*d*). The typical values of the radiative decay times for the bright exciton in quantum dots can range from 0.2–0.3 ns to 20 ns depending on the dot type [45, 46], while for the dark quantum dot exciton transitions, the times can range from 100 ns to 1–2 μs [5, 46]. It was demonstrated recently that at low temperatures, dark excitons determine the energy transfer in a dense ensemble of colloidal CdTe nanocrystals [5]. The nonradiative decay rate of the acceptor state τ_A is equal to 1 ps [47]. For the short radiative lifetime $\tau_{rad,0} = 1$ ns, the transfer is efficient ($K_{ET} > 0.5$) up to the distance $r \approx$ $\approx$ 13 nm, which is by definition the radius of the Förster process. For a larger radius, Γ_{ET} becomes smaller than Γ_{rad} (cf. solid and dotted curves in Fig. 2*c*) and the transfer is suppressed. Comparing thick and thin solid curves in panel (*c*), we can see that up to $r \lesssim 40$ nm, we have $\Gamma_{ET} \approx \Gamma_D$. This means that the transfer is purely nonradiative for $r \lesssim 40$ nm. At longer distances, when the curves deviate, the radiative correction becomes comparable with the transfer rate, although still smaller than Γ_{rad}. However, at such long distances, the transfer is quite inefficient, $K_{ET} \ll 1$. Thus, we conclude from the analysis of Fig. 2*a* and 2*c* that when the Förster process is efficient, it is nonradiative. For a longer radiative lifetime $\tau_{rad,0} = 100$ ns (Fig. 2*b* and 2*d*), the distance dependence of the transfer remains qualitatively the same, but the Förster radius shrinks to about 6 nm. The sensitivity of the Förster radius to the radiative lifetime reflects the fact that the radiative rate $\Gamma_{rad,0}$ and the Förster rate Γ_{ET} are respectively proportional to the second and fourth powers of the dipole matrix element. In Fig. 2, the dipole matrix element is chosen equal for donors and acceptors, $d_D = d_A$, and hence its increase boosts the relative efficiency of the transfer. Therefore, in order to enhance the Förster interaction between the quantum states of the same origin, it is beneficial to select the acceptor states with a radiative lifetime that is short (but still longer than the nonradiative time τ_A). The dependence of the Förster radius on the radiative lifetime is further analyzed in Fig. 3. It shows the transfer efficiencies at different donor–acceptor distances as functions of the radiative rate. The calculation confirms that the transfer at the distances beyond 10 nm requires the radiative

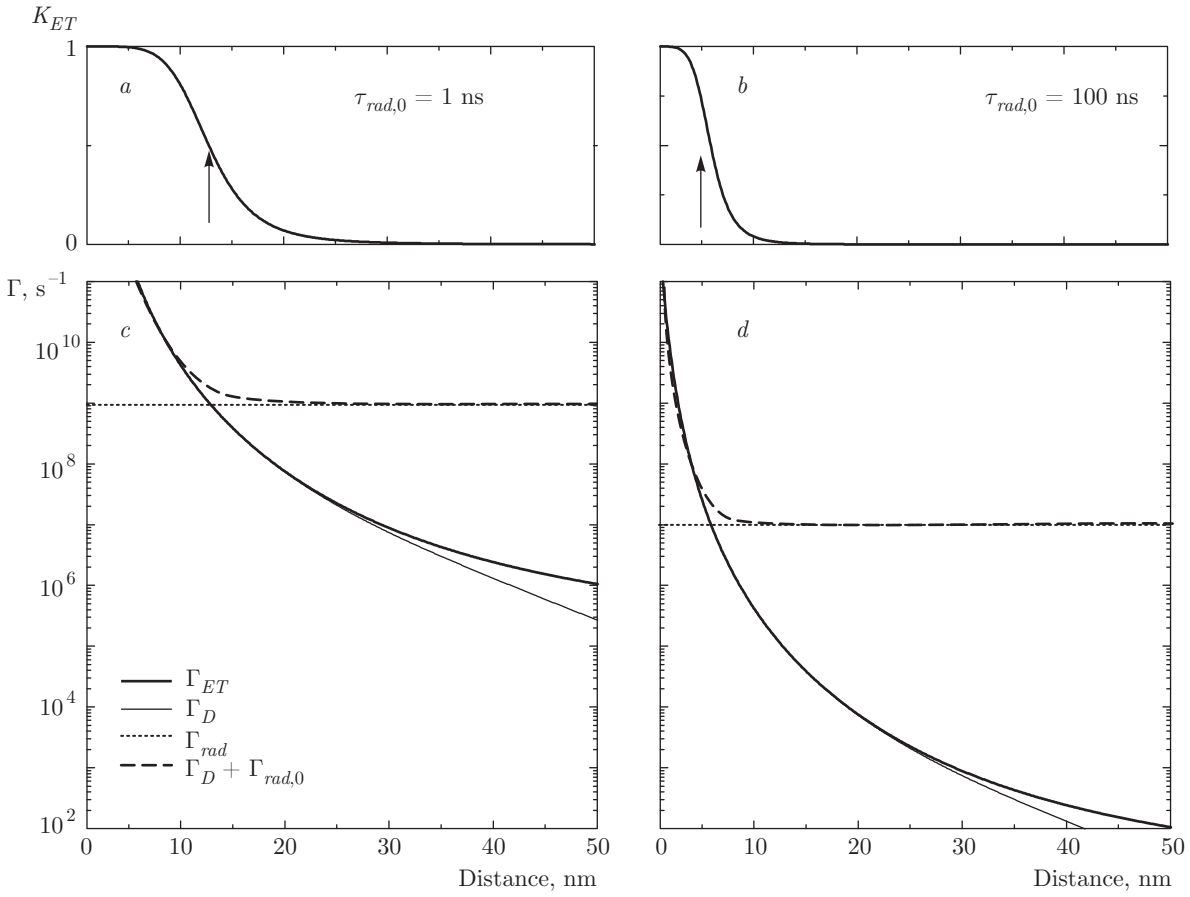

Fig. 2. (a,c) Distance dependence of the energy transfer for $\Delta = 0$ and $\tau_{rad,0} \approx 1$ ns and (b,d) $\tau_{rad,0} \approx 100$ ns. Panels (a) and (b) show the transfer efficiency K_{ET}, panels (c) and (d) show the full donor decay rates Γ_D (thin solid curves), the energy transfer rates Γ_{ET} (thick solid curves), the radiative decay rates Γ_{rad} (dotted curves), and the full donor decay rate $\Gamma_D + \Gamma_{rad,0}$ (dashed curves). Other calculation parameters are as follows: $\tau_A = 1$ ps, $\Delta = 0$, $E_D = 2$ eV, $d_D = d_A = e \cdot 0.32$ nm (a,c), $d_D = d_A = e \cdot 0.032$ nm (b,d), $\varepsilon_b = 10$. The rates are averaged over donor and acceptor orientations. Arrows in (a), (b) indicate the Förster radii where $K_{ET} = 0.5$

lifetime of the acceptor excited state to be as short as 1 ns.

Finally, in Fig. 4, we present the dependence of the transfer efficiency K_{ET} on the energy detuning Δ between the donor and the acceptor for distances $r =$ $=$ 13 nm, 8 nm, 6 nm, 4 nm (the respective thick solid, dotted, thin solid, and dashed curves) and for two different radiative lifetimes $\tau_{rad,0} = 1$ ns (a) and $\tau_{rad,0} = 100$ ns (c). The transfer efficiency is a Lorentzian function of the detuning with a maximum at $\Delta = 0$. For $\tau_{rad,0} = 1$ ns (a), the spectral range of the transfer is of the order of meV and increases at shorter donor–acceptor distances. For the long radiative lifetime $\tau_{rad,0} = 100$ ns, the spectral range strongly decreases and the transfer becomes possible only for the detuning less than 1 meV and the donor–acceptor distance $r \lesssim 5$ nm. The detuning range allowing the transfer is also inversely proportional to the nonradiative lifetime of the acceptor state $\tau_A = 1/2\gamma_A$, directly entering the overlap integral Θ in Eq. (26).

5. SUMMARY

To summarize, we have presented a theory of the Förster interaction, accounting both for the transfer of the energy from the donor to the acceptor (Förster effect) and for the antenna-like modification of the far-field donor emission by the acceptor (Purcell effect). We have demonstrated for typical parameters corresponding to the semiconductor quantum dots that the Purcell effect is negligible if the transfer efficiency is high, $K_{ET} > 0.5$. In other words, the fast transfer is

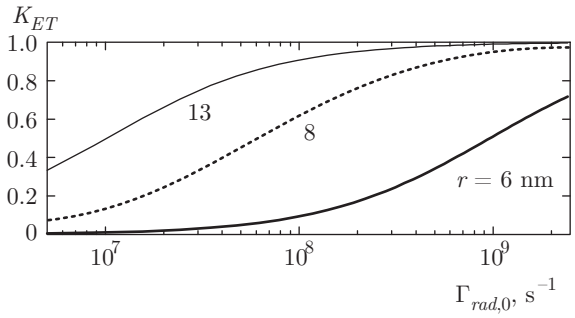

Fig. 3. Dependence of the energy transfer efficiency K_{ET} on the radiative rate $\Gamma_{rad,0}$ for different donor–acceptor distances r. The calculation has been performed for $\Delta = 0$ and the other parameters the same as in Fig. 2

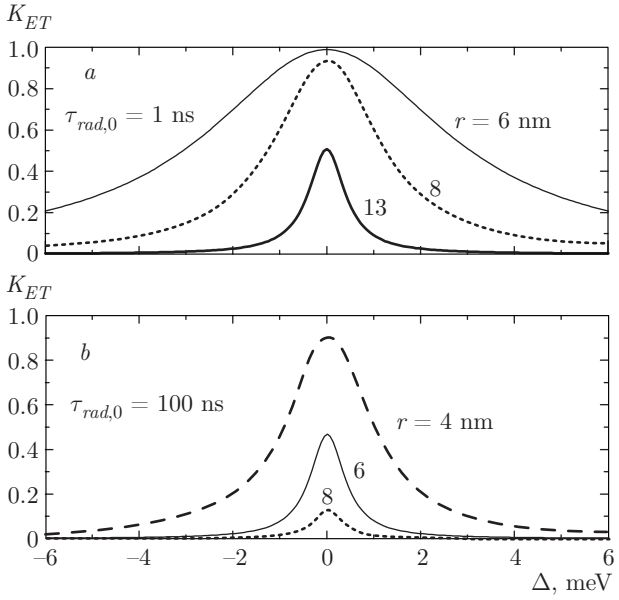

Fig. 4. Dependence of the energy transfer efficiency K_{ET} on the donor–acceptor energy detuning Δ for (a) $\tau_{rad,0} = 1$ ns and (b) $\tau_{rad,0} = 100$ ns. The thick solid, dotted, thin solid, and dashed curves correspond to the respective donor–acceptor distances $r = 13$ nm, 8 nm, 6 nm, 4 nm. The other calculation parameters are the same as in Fig. 2

purely nonradiative. The radiative corrections start to play a role only at relatively long distances $r > 40$ nm when the transfer is quenched. We have analyzed the dependence of the Förster radius on the radiative lifetime and revealed that the radius above 10 nm can be achieved only by using bright donor and acceptor excitonic states with the radiative lifetime of the order of 1 ns. In this case, the transfer takes place if the detuning between the donor and the acceptor does not exceed several meV.

While our theory is quite general, it should be stressed that the numerical results above are applicable only to the transfer in a homogeneous dielectric matrix. The competition between radiative and nonradiative transfer mechanisms in the case of a structured electromagnetic environment (plasmonic [19, 20] or dielectric [29]) requires further studies.

Stimulating discussions with V. Y. Aleshkin and M. A. Noginov are gratefully acknowledged. This work has been funded by the Russian Science Foundation (grant No. 14-22-00107). A. N. P. acknowledges the support of the "Dynasty" Foundation.

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