Resonance energy transfer and quantum dots

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The mechanism of energy transfer between quantum dots is investigated theoretically. In order to incorporate explicit account of the selection rules for absorption of circularly polarized light, a quantum electrodynamical treatment of the electronic coupling is derived. The electronic coupling is mediated by the exchange of a virtual photon, which in the far zone limit acquires real character and is circularly polarized. A rotational average expression is also obtained. The conditions by which quantum information, in terms of exciton spin orientation (total angular momentum quantum number), can be exchanged or switched through resonance energy transfer are discussed. The spectral overlap factor is considered with explicit discussion of the roles of homogeneous and inhomogeneous line broadening. It is shown that the ensemble spectral overlap is determined by the inhomogeneous line broadening dictated by sample polydispersity.
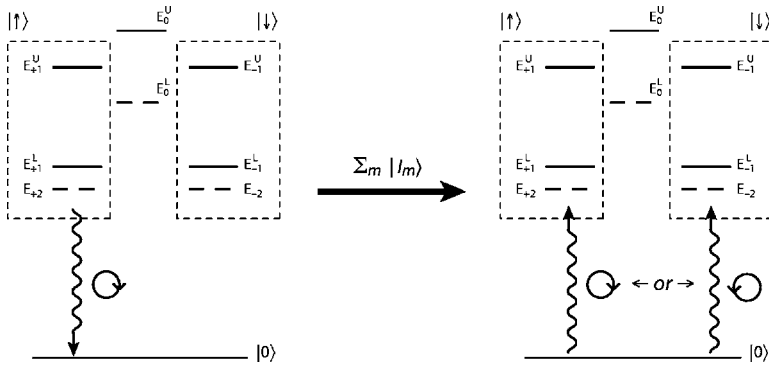
PACS number(s): 78.47.+p, 78.67.−n

I. INTRODUCTION

Resonance energy transfer (RET), often known also as electronic energy transfer (EET), is a ubiquitous photophysical process whereby an electronically excited donor molecule, atom, or in this case quantum dot (QD), transfers its excitation energy to an acceptor by a nontrivial mechanism such that the excited state lifetime of the donor is diminished.[1–8] An elegant theory that often enables the efficiency of RET to be predicted was proposed by Förster.[3] The significance of Förster's formulation is evinced by the numerous, diverse areas of study that are impacted by his paper of 1948. This predictive theory was turned on its head by Stryer,[9] who showed that distances in the range of 2 to 50 nm between molecular tags in a protein could be measured by a spectroscopic ruler known as fluorescence resonance energy transfer (FRET). Similar kinds of experiments are employed to elucidate the structure and dynamics of interfaces in blends of polymers. Photosynthetic organisms use RET to capture solar energy, using specialized light-harvesting proteins, and RET is used to tweak pixel hue and saturation in polymer-based organic light-emitting diode devices. It is not surprising to note, then, that the mechanism of RET between weakly coupled molecules is now well understood.

Since the discovery of methods for preparing luminescent semiconductor quantum dots (QDs) with narrow size dispersions, either as colloidal sols or self-assembled solid state materials, the physics of quantum confinement has been extensively studied.[10–15] Recently, examples of resonance energy transfer involving QDs have been reported[16–23] in the context of fluorophore tagging in biological systems, quantum dot lasers, and quantum computation. QDs have several characteristics that differentiate them from molecules, and such properties need to be considered to predict correctly, and to understand qualitatively, phenomena of RET involving QDs.

Although QD preparations provide narrow size distributions, the absorption and emission spectra are still significantly inhomogeneously broadened, as evident in the almost temperature-independent line widths of ensemble spectra.[24] To estimate correctly the spectral overlap integral and predict the temperature dependence of RET, the spectral inhomogeneity must be accounted for. QDs are much larger than molecules; typically ranging in diameter from 2 to 8 nm, whereas a typical molecular chromophore is only about 1 nm in size. Thus, while RET occurs between molecules that are usually separated by about 0.5 to 4 nm, QDs can approach, center-to-center, as close as only ∼4 nm, taking into account the presence of surface passivating ligands. That will surely limit the RET efficiency, depending upon the extent to which the dipole approximation for electronic coupling breaks down when QDs approach closely compared to their size.[25–27]

Finally, the selection rules for electronic transitions in QDs differ significantly from their molecular counterparts. Selection rules for absorption of circularly polarized light imply that exciton spin states can be optically oriented;[28–32] in other words, the lower, optically bright exciton states can be distinguished using circularly polarized light when the QDs are suitably oriented. In Fig. 1 the exciton fine structure that underlies the $1S_{3/2}-1S_e$ exciton band, but which is obscured by inhomogeneous line broadening in experimental spectra, is depicted.[33–36] Five of the eight states are optically bright, one of these (Ψ_0^U) being linearly polarized. The other four states can be excited according to selection rules for circularly-polarized light. For present purposes, we do not need to distinguish between Ψ_{+1}^L and Ψ_{+1}^U, which can be excited by right-circularly polarized light, or Ψ_{-1}^L and Ψ_{-1}^U, which can each be excited by left-circularly polarized light. We label each group of states $|\uparrow\rangle$ and $|\downarrow\rangle$, respectively, as indicated in Fig. 1. It is not known how to think about RET

FIG. 1. The exciton fine structure that underlies the $1S_{3/2}-1S_e$ exciton transition for CdSe QDs. Three states, drawn with dashed lines, are optically dark. Five are optically bright, one of these (Ψ_0^U) being linearly polarized. The other four states can be excited according to selection rules for circularly polarized light: the Ψ_{+1}^L and Ψ_{+1}^U states, which can be excited by right-circularly polarized light, and the Ψ_{-1}^L and Ψ_{-1}^U states, which can each be excited by left-circularly polarized light. We label each group of states enclosed in the dashed boxes $|\uparrow\rangle$ and $|\downarrow\rangle$, respectively.

between the states, for example, under what conditions can a $|\uparrow\rangle$ QD donor state sensitize either of the $|\uparrow\rangle$ and $|\downarrow\rangle$ states of an acceptor QD? That leads to the question: to what extent is optical orientation maintained after resonance energy transfer from one quantum dot to another, as shown schematically in Fig. 1 in terms of the exciton states? Such questions are particularly salient for establishing the feasibility of recent proposals for carrying out quantum computation with QD excitons.[22]

In the present work we formulate a theory for incoherent RET involving QDs, taking into account the considerations enumerated above. We discuss the ways in which QD RET differs from that familiar from studies of molecules. A unified theory for the electronic coupling that promotes RET—for example, dipole-dipole and higher multipole interactions—can be derived from quantum electrodynamics (QED). Such an approach has the conceptual advantage of considering explicitly the fate of electronic states as well as photons.[37–42] In Sec. II, we apply the QED framework to elucidate how exciton spin orientation might be retained or exchanged by RET.

II. QUANTUM AMPLITUDES

Optical pumping transfers photon angular momentum to excitons through its projection onto the wave vector direction in the crystal lattice.[28] Thus, if degenerate levels in a semiconductor are associated with different orientations of angular momentum, then circularly polarized optical excitation can preferentially excite one of these degenerate levels. Such levels include the CdSe quantum dot exciton states that we label in Fig. 1 $|\uparrow\rangle$ and $|\downarrow\rangle$. In self-assembled QDs these states can be photoselected because the QD growth is oriented with the host crystal lattice. On the other hand, linear absorption cannot optically select the $|\uparrow\rangle$ and $|\downarrow\rangle$ states in rotationally averaged QD ensembles.[44] To understand how optical orientation—that is, the total angular momentum of the exciton—is transferred by RET, it is useful to be able to consider explicitly the polarization character of the virtual photon transmitted from donor to acceptor, as we show in the following section. We explicitly consider a pair of QDs with a well-defined mutual orientation and separation, as depicted in Fig. 2. The QD that is initially photoexcited is arbitrarily labeled A, while the acceptor is labeled B.

A. Derivation using QED

A quantum electrodynamical (QED) framework has proven to be highly useful in the description and analysis of resonance energy transfer (RET).[37–42] In particular, QED provides a clear conceptual format that makes apparent the role of the donor and acceptor optical selection rules in mediating exchange of excitation. The excitation is transmitted via a virtual photon at close separations, while at large separations (the far zone), the exchanged photon acquires real character. RET rate expressions thus extrapolate naturally between near and far zone limits.[38] Similarly medium effects can be considered with respect to their action on the transmitted photon.[45] We employ the QED formalism here in order to describe explicitly the circular polarization of an exchanged photon in RET between quantum dots. Thus we are able to elucidate whether oriented exciton spin states may be transmitted from one quantum dot to another by RET. In this section we obtain the electronic coupling matrix element that
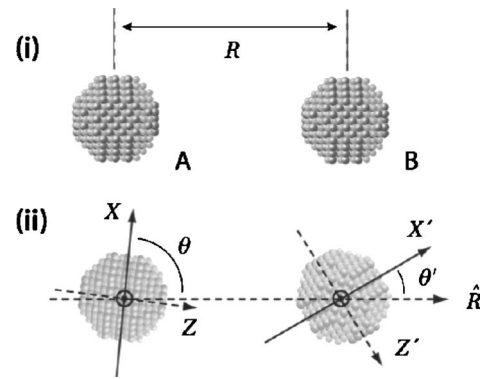

FIG. 2. (i) A pair of quantum dots A and B with center-to-center separation R. The donor is taken to be the QD labeled A. The QDs may be identical in size, otherwise typically A would be smaller than B. (ii) Coordinate system used to determine the orientation factors. We define an axis system for a quantum dot pair such that, for the donor plane normal to the crystal $\hat{Z}$ axis, $\hat{X}$ makes an angle θ with the donor-acceptor separation vector $\vec{R}$, and $\hat{Y}$ makes an angle ϕ with $\vec{R}$. Analogous angles and the axis system for the acceptor quantum dot are defined such that $\hat{X}'$ makes an angle θ' with the acceptor-donor separation vector $\vec{R}$, and $\hat{Y}'$ makes an angle ϕ' with $\vec{R}$. In the diagram $\hat{Y}$ and $\hat{Y}'$ emerge from the plane of the page.

effects the excitation transfer, further assuming the dipole approximation for the coupling, as in Förster theory. The dipole approximation might be questioned, but that does not affect the conclusions of our analysis, which focuses on orientation effects.

We consider here a system comprised of two quantum dots (QDs), Fig. 2. The initial state of the system is a photoexcited QD, the donor, in an exciton state $\alpha = |\uparrow\rangle$ or $|\downarrow\rangle$ as defined in Fig. 1 labeled A^α, a ground-state acceptor QD B^0, and an unoccupied radiation field. This initial state, and the corresponding final state whereupon the excitation has been transferred to the acceptor QD are written, respectively, as

$$|i\rangle = |A^\alpha B^0; 0(\mathbf{p}, \lambda)\rangle \qquad (1)$$

and

$$|f\rangle = |A^0 B^\beta; 0(\mathbf{p}, \lambda)\rangle. \qquad (2)$$

RET from $|i\rangle$ to $|f\rangle$ is promoted by the interaction Hamiltonian, which in the electric dipole approximation takes the form

$$H_{\text{int}} = -\epsilon_0^{-1} \sum_\xi \vec{\mu}(\xi) \cdot \mathbf{d}^\perp(\mathbf{R}_\xi), \qquad (3)$$

where the electric dipole operator $\vec{\mu}(\xi)$ operates on QD ξ and the transverse electric field displacement operator $\mathbf{d}^\perp(\mathbf{R}_\xi)$ acts at position $\mathbf{R}_\xi$ on the radiation field. It is written as the mode expansion

$$\mathbf{d}^\perp(\mathbf{R}_\xi) = i \sum_{\mathbf{p},\lambda} \left(\frac{\epsilon_0 \hbar c p}{2V} \right)^{1/2} [\mathbf{e}^{(\lambda)} a^{(\lambda)}(\mathbf{p}) e^{i\mathbf{p}\cdot\mathbf{R}_\xi}$$
$$- \overline{\mathbf{e}}^{(\lambda)} a^{\dagger(\lambda)}(\mathbf{p}) e^{-i\mathbf{p}\cdot\mathbf{R}_\xi}], \qquad (4)$$

where $\mathbf{e}^{(\lambda)}$ is the polarization vector of a virtual photon with wave vector $\mathbf{p}$ and polarization λ, and $\overline{\mathbf{e}}^{(\lambda)}$ is its complex conjugate. $a^{(\lambda)}(\mathbf{p})$ [$a^{\dagger(\lambda)}(\mathbf{p})$] is the annihilation (creation) operator for a virtual photon, and V is an arbitrary quantization volume. It may be noted that we employ the vacuum formulation of the electromagnetic field expansion. The modifications to the character of the virtual photon coupling that arise in connection with propagation through a refractive and dissipative medium lead to a slightly modified form of the ensuing results. In our present aim to elucidate the fundamental physics we retain the simplicity of the vacuum formulation; for the means to incorporate the necessary media corrections, see Ref. 43. The additional consequences of dielectric screening are considered later, in Sec. III.

The quantum amplitude for RET is calculated according to second-order perturbation theory, where the intermediate states involve virtual photon creation to give the intermediate states $|I_1\rangle = |A^0 B^0; 1(\mathbf{p}, \lambda)\rangle$ and $|I_2\rangle = |A^\alpha B^\beta; 1(\mathbf{p}, \lambda)\rangle$, such that

$$M_{fi} = \sum_m \frac{\langle f|H_{\text{int}}|I_m\rangle \langle I_m|H_{\text{int}}|i\rangle}{E_i - E_{I_m}}. \qquad (5)$$

The summation in Eq. (5) is effected for the two forms of intermediate states $|I_1\rangle$ and $|I_2\rangle$. For each case, the donor and acceptor states are fully determined, and the virtual state energy summation is effected through an integration over the

continuum of virtual photon wave vectors, as usual.[37] We thereby obtain

$$M_{fi}^{e\text{-}e} = \frac{1}{16\pi^3 \epsilon_0} \int d\mathbf{p}^3 p \left\{ \frac{[\overline{\mu}^{0\alpha} \cdot \overline{\mathbf{e}}^{(\lambda)}(\mathbf{p})][\mu^{\beta 0} \cdot \mathbf{e}^{(\lambda)}(\mathbf{p})] e^{i\mathbf{p}\cdot\mathbf{R}}}{k - p} \right.$$
$$\left. + \frac{[\overline{\mu}^{0\alpha} \cdot \mathbf{e}^{(\lambda)}(\mathbf{p})][\mu^{\beta 0} \cdot \overline{\mathbf{e}}^{(\lambda)}(\mathbf{p})] e^{-i\mathbf{p}\cdot\mathbf{R}}}{-k - p} \right\}, \qquad (6)$$

where the energy of the transferred photon is $\hbar c k$. The bar indicates complex conjugate. The integrand in the first term of Eq. (6) has a singularity but the integral does not diverge. Customarily secured by contour integration, the result is well known in connection with resonance energy transfer—see, for example, Refs. 37–40. (If the usual assumptions that are taken to ensure well-behaved long-range form are put aside, the integration can be resolved by other means, and some interesting subsidiary issues arise. These have recently been analyzed in detail in Ref. 41.)

According to the zinc blende optical selection rules, the quantum dot dipole transition moments for transitions from the ground to the $|\uparrow\rangle$ and $|\downarrow\rangle$ states are $\vec{\mu}_+ = (\mu_x + i\mu_y)/\sqrt{2}$ and $\vec{\mu}_- = (\mu_x - i\mu_y)/\sqrt{2}$, respectively. Note that we assign electronic transitions explicitly with complex conjugate transition moments when appropriate so that their complex character is carried through the calculation correctly. In this work we effect the polarization sum in terms of circularly polarized light, so that $\lambda = L$ or R, and

$$\mathbf{e}^{(L/R)} = \frac{1}{\sqrt{2}} (\hat{\mathbf{i}} \pm i\hat{\mathbf{j}}) \qquad (7)$$

and we use the identity

$$e_i^\lambda(\mathbf{p}) \overline{e}_j^\lambda(\mathbf{p}) = \frac{1}{2} (\delta_{ij} - \hat{p}_i \hat{p}_j - i\varepsilon_{ijk} \hat{p}_k). \qquad (8)$$

We assume an initial optical orientation of the donor QD, for example, such that it is initially in the state $|\uparrow\rangle$. According to the relative orientations of the donor and acceptor QDs, we can identify four contributions to the coupling matrix element

$$M_{fi}^{e\text{-}e} = M^{(a)} + M^{(b)} + M^{(c)} + M^{(d)}. \qquad (9)$$

The first two terms are evaluated according to

$$M^{(a,b)} = \frac{1}{32\pi^3 \epsilon_0} \int d\mathbf{p} (\delta_{ij} - \hat{p}_i \hat{p}_j) p$$
$$\times \left\{ \frac{\overline{\mu}_j^{0\alpha} \mu_i^{\beta 0} e^{i\mathbf{p}\cdot\mathbf{R}}}{k - p} + \frac{\overline{\mu}_i^{0\alpha} \mu_j^{\beta 0} e^{-i\mathbf{p}\cdot\mathbf{R}}}{-k - p} \right\} \qquad (10)$$

$$= \frac{1}{32\pi^3 \epsilon_0} \mu_i^{0\alpha} \overline{\mu}_j^{\beta 0} (-\nabla^2 \delta_{ij} + \nabla_i \nabla_j) \int dp \, d\Omega \, p$$
$$\times \left\{ \frac{e^{i\mathbf{p}\cdot\mathbf{R}}}{k - p} + \frac{e^{-i\mathbf{p}\cdot\mathbf{R}}}{-k - p} \right\} \qquad (11)$$

the difference between them being that for $M^{(a)}$ spin is conserved through the RET, so that if $\alpha = |\uparrow\rangle$ then $\beta = |\uparrow\rangle$. (Note that α and β label exciton states which include the states

defined in Fig. 1 labeled $\uparrow$ and $\downarrow$, not to be confused with electron spin.) On the other hand, $M^{(b)}$ describes a RET process whereby the exciton spin state is flipped; if $\alpha=|\uparrow\rangle$ then $\beta=|\downarrow\rangle$. There is a similar relationship between $M^{(c)}$ and $M^{(d)}$, which are obtained from

$$M^{(c,d)} = \frac{-i}{32\pi^3\epsilon_0} \int d\mathbf{p}^3 \varepsilon_{ijk}\hat{p}_k p \left\{ \frac{\bar{\mu}_j^{0\alpha}\mu_i^{\beta0}e^{i\mathbf{p}\cdot\mathbf{R}}}{k-p} + \frac{\bar{\mu}_i^{0\alpha}\mu_j^{\beta0}e^{-i\mathbf{p}\cdot\mathbf{R}}}{-k-p} \right\} \tag{12}$$

$$= \frac{-i}{32\pi^3\epsilon_0} \bar{\mu}_i^{0\alpha}\mu_j^{\beta0}\varepsilon_{ijk} \int d\mathbf{p}^3 \left(\frac{p_k}{k^2-p^2} \right)$$
$$\times \{k(e^{i\mathbf{p}\cdot\mathbf{R}} + e^{-i\mathbf{p}\cdot\mathbf{R}}) + p(e^{i\mathbf{p}\cdot\mathbf{R}} - e^{-i\mathbf{p}\cdot\mathbf{R}})\}. \tag{13}$$

This matrix element is related to that for $E1$-$M1$ coupling.[42] By contour integration we establish that $M^{(c,d)}=0$.

For the first two terms of M_{fi}^{e-e} we obtain

$$M^{(a)} = M^{(b)} = \frac{1}{2}\bar{\mu}_i^{0\alpha}V_{ij}(k,\mathbf{R})\mu_j^{\beta0}, \tag{14}$$

where $V_{ij}(k,\mathbf{R})$ is the standard $E1$-$E1$ retarded resonance coupling tensor

$$V_{ij}(k,\mathbf{R}) = \frac{e^{ikR}}{4\pi\epsilon_0 R^3}[(1-ikR)(\delta_{ij} - 3\hat{R}_i\hat{R}_j)$$
$$- (kR)^2(\delta_{ij} - \hat{R}_i\hat{R}_j)]. \tag{15}$$

One of the key features of Eq. (15), of particular relevance to the issues to be examined below, is that its short- and long-range limits (traditionally but perhaps misleadingly identified as "radiationless" and "radiative") assume an identical orientational dependence if either the donor or acceptor transition moment lies orthogonal to the displacement vector $\mathbf{d}^\perp(\mathbf{R})$. The significance of this is that, although the power-law dependence on the magnitude of the displacement is different, the character of the energy transfer in the near zone is in certain key respects the same as that associated with "real" photon exchange.

To calculate the orientation dependence for the electronic coupling matrix element it is important to account for complex conjugate transition moments such that an absorptive transition from $|0\rangle$ to $|m\rangle$ has the transition dipole moment $\mu=\langle m|H_{int}|0\rangle$, while an emissive transition from $|m\rangle$ to $|0\rangle$ has the transition dipole moment $\bar{\mu}=\langle 0|H_{int}|m\rangle$. To consider explicitly the selection rules for virtual photon emission and absorption we carried out the polarization sum explicitly with respect to circularly polarized photon exchange. However, the same final result is obtained by using the usual polarization sum using the identity

$$\sum_\lambda e_\alpha^{(\lambda)}(\mathbf{k})\bar{e}_\beta^{(\lambda)}(\mathbf{k}) = \delta_{\alpha\beta} - \hat{k}_\alpha\hat{k}_\beta, \tag{16}$$

which accommodates complex polarization vectors.

B. Near zone result

In the near zone limit, $kR\ll 1$, the quantum amplitude simplifies to

$$M^{e-e} \approx \frac{\kappa|\mu^{0\alpha}||\mu^{\beta0}|}{4\pi\epsilon_0 R^3}, \tag{17}$$

where R is the center-to-center separation between the QDs and the orientation factor κ is given by

$$\kappa = \hat{\bar{\mu}}_i^{0\alpha}(\delta_{ij} - 3\hat{R}_i\hat{R}_j)\hat{\mu}_j^{\beta0}. \tag{18}$$

We envision two distinct cases of RET involving quantum dots: (i) RET that transfers the spin state from donor to acceptor, $|\uparrow\rangle\rightarrow|\uparrow\rangle$ (or $|\downarrow\rangle\rightarrow|\downarrow\rangle$) and (ii) RET that flips the spin state, $|\uparrow\rangle\rightarrow|\downarrow\rangle$ (or $|\downarrow\rangle\rightarrow|\uparrow\rangle$). These processes are differentiated by their orientation factors.

Defining an axis system for the quantum dot pair, Fig. 2, such that, for the donor plane normal to the crystal $\hat{Z}$ axis, $\hat{X}$ makes an angle θ with the donor-acceptor separation vector $\vec{R}$, and $\hat{Y}$ makes an angle ϕ with $\vec{R}$. Analogous angles and the axis system for the acceptor quantum dot are defined such that $\hat{X}'$ makes an angle θ' with the acceptor-donor separation vector $\vec{R}$, and $\hat{Y}'$ makes an angle ϕ' with $\vec{R}$.

We find for case (i)

$$\kappa_{\uparrow\uparrow} = \cos(\theta-\theta') + \cos(\phi-\phi')$$
$$- 3(\cos\theta - i\cos\phi)(\cos\theta' + i\cos\phi'), \tag{19}$$

$$\kappa_{\downarrow\downarrow} = \cos(\theta-\theta') + \cos(\phi-\phi')$$
$$- 3(\cos\theta + i\cos\phi)(\cos\theta' - i\cos\phi'), \tag{20}$$

while for case (ii)

$$\kappa_{\uparrow\downarrow} = \cos(\theta-\theta') - \cos(\phi-\phi')$$
$$- 3(\cos\theta + i\cos\phi)(\cos\theta' + i\cos\phi'), \tag{21}$$

$$\kappa_{\downarrow\uparrow} = \cos(\theta-\theta') - \cos(\phi-\phi')$$
$$- 3(\cos\theta - i\cos\phi)(\cos\theta' - i\cos\phi'). \tag{22}$$

C. Far zone result

For completeness we consider the matrix element in the case when the donor-acceptor interaction is mediated by exchange of a real photon; a situation relevant only for very large donor-acceptor separations. When $kR\gg 1$, then

$$M^{e-e} \approx \frac{-\kappa'k^2 e^{ikR}|\mu^{0\alpha}||\mu^{\beta0}|}{4\pi\epsilon_0 R}, \tag{23}$$

where the orientation factor κ' is given by

$$\kappa' = \hat{\bar{\mu}}_i^{0\alpha}(\delta_{ij} - \hat{R}_i\hat{R}_j)\hat{\mu}_j^{\beta0}. \tag{24}$$

The ensuing results are of similar form to the near-zone results given by Eqs. (17) and (18), but differing in three respects: (i) the distance dependence is modified from R^{-3} to k^2R^{-1}, correctly generating an inverse square law for the transfer rate; (ii) the emergence of the phase factor e^{ikR} signifies the absorption of a photon that has propagated from the donor; (iii) the orientation factors differ only from those given in Eqs. (19)–(22) by removal of the factor 3 in each

case—here signifying complete transversality of the radiation field with respect to **R**.

III. RESONANCE ENERGY TRANSFER RATES

When the donor and acceptor are weakly coupled electronically relative to their coupling to the condensed phase bath (incoherent energy transfer), the rate of RET is obtained as the product of an electronic matrix element squared and a "spectral overlap" factor.[2,6–8] The former factor is the quantum amplitude derived in the previous section, while the latter factor measures the overlap of donor emission and acceptor absorption. This is the usual case of energy transfer observed experimentally and can generally be justified, despite the weak electron-phonon coupling characteristic of QDs, because the electronic coupling is weak as a result of their large size and hence center-to-center separation.

A characteristic of QDs is that samples have a size distribution, and consequently the ensemble optical properties are spectrally broadened because of the dependence of optical gap on QD size. Usually this inhomogeneous line broadening needs to be considered separately from homogeneous line broadening when calculating the spectral overlap factor. Förster theory provides a means of estimating the spectral overlap factor directly from experimental spectra. However, because QD photoluminescence and absorption spectra are strongly inhomogeneously broadened, this procedure may not work.[48,49]

The inhomogeneous line broadening present in the donor emission spectrum and that present in the acceptor absorption spectrum leads to individually ensemble averaged quantities. The spectral overlap factor J that relates to RET is also an ensemble average quantity,[46,47] but it is not necessarily related in a simple way to the overlap of the ensemble averaged emission and absorption spectra. That is, usually, $J = \int_0^\infty d\epsilon \langle f(\epsilon) a(\epsilon) \rangle \neq \int_0^\infty d\epsilon \langle f(\epsilon) \rangle \langle a(\epsilon) \rangle$, where the angle brackets denote ensemble averaging over inhomogeneous line broadening, $f(\epsilon)$ and $a(\epsilon)$ are the homogeneous line shapes deconvolved from the donor emission and acceptor absorption spectra respectively. We investigate these matters below.

An expression for the rate of energy transfer from a donor in electronic state α to the electronic state β of an acceptor is given by

$$k_{ij} = \frac{2\pi}{\hbar} \left\langle \int_0^\infty d\epsilon P_\alpha |DM_{\alpha\beta}^{e\text{-}e}|^2 J_{\alpha\beta}(\epsilon) \right\rangle. \qquad (25)$$

The angle brackets denote that an ensemble average is taken over many donor-acceptor pairs so as to account for static disorder in the QD transition energies relative to the mean. The coefficient D accounts for dielectric screening of the electronic coupling, and P_α is a normalized Boltzmann weighting factor for the contribution of α to the thermalized donor state

$$P_\alpha = \frac{\exp[(\epsilon_{\alpha=1} - \epsilon_\alpha)/kT]}{\sum_\alpha \exp[(\epsilon_{\alpha=1} - \epsilon_\alpha)/kT]}. \qquad (26)$$

The states α and β include each of the optically allowed transitions. For small quantum dots we should explicitly ac-

count for the fine structure within the first absorption band.[33,34]

The Förster-type spectral overlap is defined in terms of area normalized donor and acceptor emission $f_\alpha(\epsilon)$ and absorption $a_\beta(\epsilon)$ line shapes[2,3,6,8]

$$J_{\alpha\beta}(\epsilon) = a_\alpha(\epsilon) f_\beta(\epsilon). \qquad (27)$$

Specifying single donor and acceptor states and evaluating the spectral overlap as $J = \int_0^\infty d\epsilon J_{\alpha\beta}(\epsilon)$, Eq. (25) is rewritten more succinctly as

$$k = \frac{2\pi}{\hbar} |DM^{e\text{-}e}|^2 \langle J \rangle, \qquad (28)$$

where $D \approx 1/n^2$, n is the medium refractive index. We have assumed that $M^{e\text{-}e}$ varies little through the QD size distribution; then we can separate the electronic and nuclear factors and ensemble average just over the spectral overlap $\langle J \rangle$.

The spectral overlap factor needs to be considered carefully for quantum dots owing to the large inhomogeneous line broadening. Parameters describing the homogeneous line broadening are collected in a line shape function $g(t)$, which is used to reconstruct the spectra,[50] and then to obtain the spectral overlap. The absorption and emission line shapes, free of inhomogeneous line broadening, are given by[50]

$$a(\epsilon) \propto \mathrm{Re} \int_0^\infty dt \exp[i(\omega - \omega_\beta)t - g(t)], \qquad (29)$$

$$f(\epsilon) \propto \mathrm{Re} \int_0^\infty dt \exp[i(\omega - \omega_\alpha + 2\lambda)t - g^*(t)], \qquad (30)$$

where the constant of proportionality is obtained through the condition of area normalization.

The spectral line shape of quantum dots is primarily dictated by coupling of the exciton to quantized acoustic phonons.[51] In that case, and assuming a short-time approximation,[52] the line shape function $g(t)$ is

$$g(t) \approx \frac{1}{2}\Delta^2 t^2, \qquad (31)$$

where Δ^2 is directly related to the Stokes shift 2λ by $\Delta^2 = 2k_B T \lambda / \hbar$. This expression is quite different from the form of the line shape function for molecular systems owing to the distinctly different baths that couple to the elementary excitations. The values of Δ depend on the size and composition of the quantum dot, but a useful average value for $T \sim 100$ K is $\Delta \approx 0.02$ fs^{-1}. Given that the standard deviation of the inhomogeneous line broadening is σ_d for the donor and σ_a for the acceptor, assuming Gaussian distributions $G(\delta_\alpha)$ and $G(\delta_\beta)$ of offsets δ_α and δ_β from the mean transition energies, we finally obtain

$$\langle J \rangle = \int d\epsilon \int \int d\delta_\alpha d\delta_\beta f(\epsilon) G(\delta_\alpha) a(\epsilon) G(\delta_\beta), \qquad (32)$$

where we have determined for typical samples that $\sigma_d \approx \sigma_a \approx 68$ meV for CdSe colloidal quantum dots.[53] This expres-

sion can be simplified by incorporating the inhomogeneous line broadening into the line shape function

$$g'(t) \approx \frac{1}{2}\Delta^2 t^2 + \frac{1}{2}(2\pi\sigma)^2 t^2, \qquad (33)$$

whereupon it is apparent that the homogeneous line broadening is overwhelmed by the inhomogeneous broadening in the spectral overlap, which means that the RET rate between quantum dots does not depend on the precise details of homogeneous line broadening and is independent of temperature.

Using Eq. (15), the RET rate is found to be

$$k = \frac{2\pi}{\hbar n^4}\langle J \rangle \bar{\mu}_i^{0\alpha}\mu_k^{0\alpha}V_{ij}(k,\mathbf{R})\bar{V}_{kl}(k,\mathbf{R})\mu_j^{\beta 0}\bar{\mu}_l^{\beta 0}. \qquad (34)$$

For colloidal dots, the orientational averaged situation is of interest. In the near zone, on isotropic averaging, we obtain

$$k = \frac{1}{12\pi^2\epsilon_0^2 R^6}\langle J \rangle |\mu^{0\alpha}|^2|\mu^{\beta 0}|^2 \qquad (35)$$

which is similar to the usual rotationally averaged expression. This equation applies to pairs of quantum dots or to a quantum dot and molecule. If the concentration of quantum dots is high, then the random distribution of donor-acceptor orientations becomes skewed, and a static model for the orientational averaged orientation factor may be more realistic.[54]

IV. DISCUSSION

A. Optical orientation via RET

Various schemes have been proposed for carrying out quantum computation using coupled excitons in an organization of quantum dots.[20–22] Those proposals make use of the high oscillator strength and discrete, size-tunable energy of quantum dot exciton transitions that can be switched rapidly using optical excitation. It is also desirable to make use of additional quantum information that can be instilled into quantum dots in the form of the total angular momentum of the quantum dot exciton state. Specific exciton spin states can be prepared using circularly polarized excitation—optical orientation. The question remains, can the quantum spin state of a exciton be transmitted or flipped through resonance energy transfer between suitably organized quantum dots?

Typical self-assembled quantum dots are grown in a plane with their c axis normal to the plane. The present work shows that they do not exchange circularly polarized light, and resonance energy transfer is governed by separation but not orientation. Hence quantum information is lost through RET. On the other hand, if quantum dots are grown in a column,[18] then quantum information can be manipulated. The plots in Fig. 3 show the effect of rotating one quantum dot relative to another through $\phi=0$ to 2π, assuming the electronic coupling to be real. When $\phi=3\pi/2$ the geometry causes the exciton spin to be flipped during RET, whereas when $\phi=\pi/2$ the exciton orientation is transmitted from one
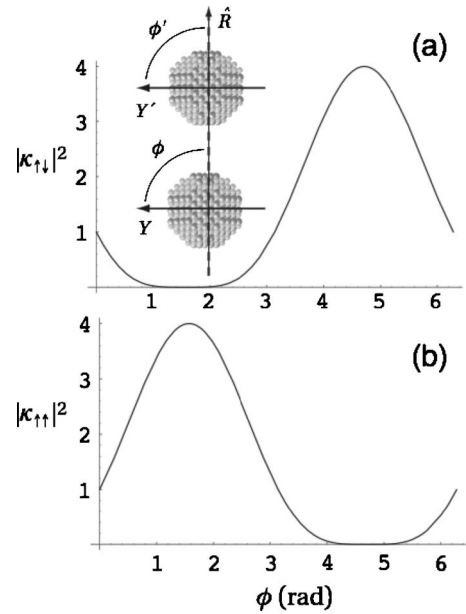

FIG. 3. Plots showing the variation of (a) $|\kappa_{\uparrow\downarrow}|^2$ and (b) $|\kappa_{\uparrow\uparrow}|^2$ as a function of the angle ϕ defining a rotation of one quantum dot relative to another. Note that for the parallel case $\phi=\pi/2$. The other angles are fixed: $\theta=\theta'=\phi'=\pi/2$.

quantum dot to another. Energy migration down a column of quantum dots oriented in a common direction therefore corresponds to spatial hopping of the exciton with retention of spin orientation. Physically, this effect signifies conservation of spin angular momentum about the axis defined in common by the direction of excitation transfer and the local columnar morphology.

B. RET rates between colloidal QD pairs

The mutual orientation of colloidal quantum dots cannot easily be controlled, so the oriently averaged rate expression is employed. In that case, the quantum dot selection rules are not explicitly evident and optical orientation is not transferred throughout an ensemble. A remaining challenge concerning the electronic coupling is to go beyond the dipole-dipole approximation. A convenient way to do that is to calculate the interaction between quantum dot transition densities,[26] although obtaining those transition densities is a computational challenge.

To quantify typical spectral overlaps for a model CdSe quantum dot system we begin with a simple modeling of the absorption spectrum of the acceptor quantum dot, in this case a 4.0 nm CdSe sample. The absorption spectrum was simulated using Eq. (29), including the first four electronic states and an artificial fifth band, and is shown in Fig. 4 compared to experimental data for CdSe in polybutylmethacrylate at 4 K. We use transition energies of 2.32, 2.51, 2.68, and 2.83 eV, corresponding to relative transition dipole magnitudes of 1.1, 0.675, 0.7, and 1.1 arb. units and population relaxation (T_1) times of 20 ns, 20 ns, 7 ps, and 2.5 ps. We also use $\Delta=0.02$ fs^{-1} and find that $\sigma_a=550$ cm^{-1}. The model donor photoluminscence spectra are calculated using Eq. (30) for various energies relative to the donor absorption,
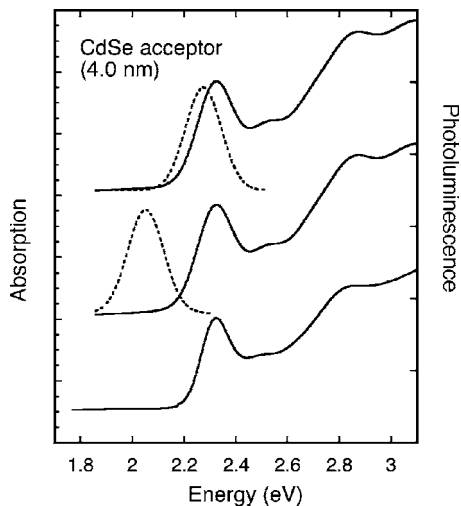
FIG. 4. The lower curve is a plot of experimental measurement of the absorption spectrum of CdSe colloidal quantum dots (4.0 nm average diameter) in a polymer film at 4 K. The upper two absorption curves (for the resonance energy transfer acceptor) are simulated using Eq. (29). The dashed curves represent two of the donor emission spectra considered in our calculations.

two of which are shown as the dashed lines in Fig. 4.

In Fig. 5 we plot calculated ensemble average spectral overlaps $\langle J \rangle$, from Eq. (27), as a function of donor photoluminescence energy relative to the acceptor absorption spectrum. We find that, when the donor photoluminescence overlaps well with the absorption, $\langle J \rangle \approx 1. \times 10^{-4}$ cm, which is more than an order of magnitude smaller than that predicted by Crooker *et al.* Energy transfer rates from Eq. (25), using the electronic coupling suggested by Crooker *et al.*,[16] are also plotted in Fig. 5, and these are seen to follow the trend of the spectral overlap. However, the actual magnitude of the rate is then strongly influenced by the choice of electronic coupling.
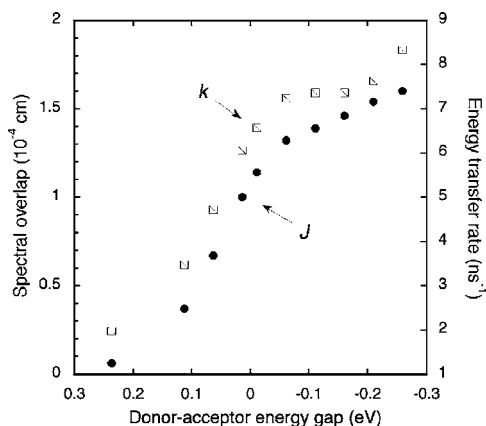

FIG. 5. Plot of the ensemble averaged spectra overlap and the energy transfer rate calculated as a function of donor-acceptor energy gap, representing a variation in the average size of the donor quantum dots.

On the other hand, if we inspect individual pairs of quantum dots within the ensemble, a great variation in energy transfer rates is evident. For example, for four donor-acceptor quantum dot pairs randomly chosen from the ensemble, the corresponding spectral overlap integrals were calculated to be 4.89×10^{-4}, 1.32×10^{-5}, 6.49×10^{-6}, and 1.19×10^{-4} cm. This observation poses a challenge to single-molecule energy transfer experiments using quantum dot pairs because the spectral overlap is so strongly dependent on the inhomogeneous broadening, the energy transfer rate cannot be predicted for individual pairs of dots unless the spectral overlap is measured simultaneously. In this sense, the analogy drawn by Crooker *et al.*[16] to the light-harvesting complex LH2 from photosynthetic purple bacteria[55] can be extended. RET within the LH2 antenna complex is strongly affected by an inhomogeneous distribution of transition frequencies for the molecules involved.[56]

V. CONCLUSIONS

In analyzing the mechanism for resonant energy transfer (RET) between quantum dots (QDs), it proves possible to identify a number of significant differences from the corresponding process in molecular systems—beyond the commonly much narrower distribution of transition frequencies cited above. Important distinctions between molecular and quantum dot light harvesting arrays are associated with fundamental differences in character of the mechanism promoting RET. In this work, the adoption of a fully quantized framework for the theory has elicited the involvement of intrinsic QD properties in the character of the energy propagation—an involvement that affords an opportunity to control exciton spin orientation or exchange. It turns out that for randomly oriented QDs, and under the assumption that the dipole approximation provides a meaningful description of the electronic coupling, a Förster-type rate expression provides a good description of the ensemble RET rate.

An important difference between QDs and molecules lies in the optical selection rules, which we considered explicitly using a quantum electrodynamical analysis. Key features have been established in the resonance energy transfer mechanism for spin retention between quantum dots. As observed in Sec. II A, the case of energy transfer between quantum dots whose complex transition moments lie in a plane orthogonal to the transfer direction is especially significant. This is because this system has a unique physical character in which, although the power law on distance changes as expected between near-zone and far-zone displacements, the symmetry properties are the same in each region. This in turn has an important physical consequence, even though the long-range behavior is of little interest from an application viewpoint; it is clear that angular momentum must in that case be conserved about the propagation direction of the photon—which coincides with the mutual displacement vector of the two quantum dots. Thus it transpires that the same feature operates in the technically important near-zone region, even though the coupling cannot in this case be ascribed to real photon propagation. Thus it is, that energy migration down a column of quantum dots with a

common orientation (Sec. IV) preserves spin information, absolutely. The observation of spin flipping in transfer between alternately inverted quantum dots is another manifestation of the same principle.

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