

Examining Förster Energy Transfer for Semiconductor Nanocrystalline Quantum Dot Donors and Acceptors

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Excitation energy transfer involving semiconductor quantum dots (QDs) has received increased attention in recent years because their properties, such as high photostability and size-tunable optical properties, have made QDs attractive as Förster resonant energy transfer (FRET) probes or sensors. An intriguing question in FRET studies involving QDs has been whether the dipole approximation, commonly used to predict the electronic coupling, is sufficiently accurate. Accurate estimates of electronic couplings between two 3.9 nm CdSe QDs and between a QD and a chlorophyll molecule are reported. These calculations are based on transition densities obtained from atomistic semiempirical calculations and time-dependent density functional theory for the QD and the chlorophyll, respectively. In contrast to the case of donor–acceptor molecules, where the dipole approximation breaks down at length scales comparable to the molecular dimensions, we find that the dipole approximation works surprisingly well when donor and/or acceptor is a spherical QD, even at contact donor–acceptor separations. Our conclusions provide support for the use of QDs as FRET probes for accurate distance measurements.

The special properties of semiconductor nanocrystalline quantum dots (QD), such as high photostability, size-tunable optical properties, and the possibility to functionalize their surfaces with particular ligands have inspired a breadth of research,^{1–6} including

from eqs 1 and 2, assuming that the D and A electron densities do not overlap and do not distort each other.

Traditionally, the transition densities are expanded as a multipole series, and then eq 2 would be evaluated as the interaction between the multipoles corresponding to D and A³⁷

$$V_s^{(\text{multipole})} = V_{\text{dip-dip}} + V_{\text{dip-quad}} + V_{\text{quad-dip}} + V_{\text{dip-oct}} + V_{\text{oct-dip}} + V_{\text{quad-quad}} + \dots \quad (3)$$

The coupling $V_s^{(\text{multipole})}$ given by eq 3 reproduces the exact result of eq 2 provided that an untruncated multipole expansion is used and that the multipoles are calculated exactly from the same transition densities, that is, $\mu_{\text{eg},\alpha}^{\text{QD}} = \int r_{\alpha} \rho_{\text{eg}}^{\text{QD}}(\mathbf{r}) d\mathbf{r}$. In the classic Förster theory,³⁸ the coupling is obtained by truncating this expansion to the first term, which is an interaction between transition dipole moments. This so-called point-dipole approximation gives the characteristic R^{-6} decay of the rates

$$V_s^{(\text{multipole})} \approx V_{\text{dip-dip}} = \frac{\kappa \mu_{\text{D}}^{\text{T}} \mu_{\text{A}}^{\text{T}}}{R^3} \quad (4)$$

where $\mu_{\text{D}}^{\text{T}}/\mu_{\text{A}}^{\text{T}}$ are transition dipole moments of D and A separated by a distance R , and the orientation factor, κ , is defined in terms of the angles between transition moments and the donor–acceptor vector.¹⁷ In the case of QDs, the relevant transition moments follow selection rules for circularly polarized light^{6,39} so care needs to be taken when determining κ .¹² Often an orientational average is taken, such that $\kappa^2 \rightarrow 2/3$ is used in the rate expression.

Here we compare the EET rate obtained from the unapproximated, 3D formula of eq 2, with the multipole expansion of eq 3 and the classic point-dipole approximation of eq 4. We consider (i) two identical 3.9 nm diameter CdSe wurtzite QDs, and (ii) a CdSe QD and a nearby chlorophyll-*a* molecule (Chl). The density matrices of eq 2 for CdSe are obtained from atomistic pseudopotential calculations in a plane wave basis, whereas the density matrices for chlorophyll are obtained from time-dependent density functional calculations in a Gaussian basis. We find that in contrast to what is typically observed in EET involving two molecules, the point-dipole approximation gives an excellent estimate of electronic couplings for the three different orientations between the donor and the acceptor we consider, both for the QD–Chl and QD–QD systems, even at close-contact separations. This latter result is in agreement with a recent study of QD–QD pairs that employed semiempirical calculations based on the tight-binding Hamiltonian.²⁹

We explain the accuracy of the dipole approximation

the different orientations. In particular, we have considered (i) a face-to-face (FF) orientation ($\theta_D = -\pi/2$ and $\theta_A = -\pi/2$), (ii) a head-to-tail (HT) orientation ($\theta_D = 0$, $\theta_A = 0$), and (iii) a diagonal-like (DL) orientation (θ

