Excitation energy transfer in multichromophoric systems

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Different methods are tested for determining the excitation energy transfer rate in a model of coupled ring systems, a situation where conventional Förster theory is breaking down. The study on simple systems can help better understanding of validity and applicability of different approaches, when studying bigger systems.

Coherent multidimensional spectroscopy allows unraveling excitation energy transport in complex nature of light-harvesting systems. The interpretation of such spectra is challenging and often require theoretical modeling.

The excitation energy transfer rates can be described by the Förster resonance energy transfer (FRET)¹, which relates the transfer rate to the overlap integral of the donor's emission and acceptor's absorption spectra and the transition-dipole coupling. This theory gives an excellent description for distant chromophores in a perturbative regime, while being unable to give even a qualitative adequate picture for closely spaced multichromophoric systems, where donor and acceptor systems cannot be approximated by single total transition dipole moments. Instead the theoretical approach that takes into account collective excitation character of the donor and acceptor should be applied.

In this work we study alternative theories to FRET ^{2,3,4,5} by applying them to a phenomenological model of coupled ring systems. The analyses of the methods should give criteria of validity of theories and practical feasibility of application to large systems.



Fig.1 Phenomenological model of a coupled ring system, where blue arrows represent transition dipole moments of the chromophores lying in the plane; the red arrow represents an initially excited chromophore. The comparison of methods is based on the study of the excitation energy transfer rate from the inner ring to the outer ring.

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