chromophores. This study helps predict the properties of the entangled two photon effect in chromophores with different dipolar and quadrupolar character.

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Delocalization length in the context of biological exciton transfer processes

Kieran Fox
Charles University

Exciton delocalization in natural light harvesting structures is a well-known phenomenon, recognised as an important factor in photosynthetic excitation energy transfer efficiency. Standard attempts to define delocalization length within the dynamic environment of a protein, and over biological timescales, results in a single real number or an integer range of pigments. We argue that such a notion of delocalization is not particularly informative or characteristic of the potentially complicated connection network of pigments represented by a photosynthetic antenna. Add to this there seems to be some mixing of concepts under the term delocalization due to the ultra-fast methods of measuring it. We aim to disentangle the delocalization relating to transitions between molecules as a result of resonance coupling, from the coherent state caused by laser excitation in spectroscopic experiments. This is done by respecting the uncertainty of delocalization in time, which we show by analysing the structure of the coherent state excited by ultrashort laser pulse. We demonstrate, on a system exhibiting static disorder only, how a generalised notion of delocalization can be introduced. With this is we can give a better representation of the states, including specific pigment contributions to the delocalized states as this can be crucial to the overall function of the system. We revisit past pump-probe measurements of LH1 and LH2 as well as new 2DES spectra to reexamine the concept of delocalization and try to come to grips with what it means in biological excitation energy transfer processes.

A Step Towards a Comprehensive Steady-State Picture of Photosynthetic Solar Energy Conversion

Veljko Janković
Faculty of Mathematics and Physics, Charles University, Prague

The interpretation of oscillating experimental signals observed in ultrafast nonlinear spectroscopies [1] has been motivating vigorous interest in quantum effects in photoinduced biological processes. However, electronic dynamics triggered by natural light, which is stationary and incoherent, is generally substantially different from the one observed in pulsed laser experiments. It has been suggested that the physically correct picture of photosynthetic excitation energy transfer (EET) should be in terms of a steady state [2], which is formed when the photosynthetic antenna is continuously photoexcited and continuously delivers the excitation energy to the reaction center, in which charge separation takes place.

We study EET triggered by a low-intensity photoexcitation of an initially unexcited molecular aggregate, whose molecules interact with their unstructured local environments and which is coupled to the reaction center. We treat the aggregate–environment coupling in a numerically exact manner and extend previous theoretical treatments [3,4] by formulating the hierarchy of equations of motion (HEOM) which explicitly takes into account the photoexcitation process. We investigate the properties of the steady state arising when the aggregate is subjected to a continuous-wave excitation, while photoinduced electronic excitations can either recombine or undergo charge separation from the reaction center. The developed theoretical formalism enables us to approach questions ranging from the influence of the short-time dynamics (which is accessible in pulsed laser experiments) on the steady state to the relevance of steady-state coherences for the EET process.

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Matrix-product-state-based calculations of exciton-phonon dynamics for light-harvesting complexes

Kevin Kessing
Uni. Göttingen/MIT

Excitonic systems with one to a few dozen sites are an important and commonly studied topic in various contexts, such as quantum optics, molecular spectroscopy or the dynamics of light-harvesting complexes. However, in reality the dynamics are often strongly influenced by their coupling to the environment or internal vibrational modes. Computing such systems with non-negligible and non-perturbative interactions is a challenging problem, and oftentimes simplifications such as the Markov assumption are made to assist in such calculations. In our approach, we investigate the dynamics of excitonic oligomers with such interactions without neglecting the internal dynamics of the bath using a symmetry-adapted state-of-the-art matrix-product-state (MPS) code [1]. By employing this approach together with the analytic transformation of the bath Hamiltonian into discrete sites (TEDOPA) proposed by Martin Plenio et al. [2], we may also model non-Markovian dynamics of exciton systems with strong bath coupling. The insights gained from these analyses help us better understand the phonon-assisted transport effects in photosynthetic complexes such as the purple-photosynthetic-bacterial light-harvesting complex LH2, which exhibits a remarkably efficient energy transfer and notable symmetric structure [3].

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Pathway Analysis of Protein Electron-Transfer Reactions by Using Ab Initio Electronic Structure Calculations

Hirotaka Kitoh-Nishioka
JST-PRESTO and University of Tsukuba

We have developed a novel computational scheme [1] to analyze electron transfer (ET) reactions in protein. Our scheme combines the fragment molecular orbital (FMO) method with an electron tunneling current analysis, which enables an efficient first-principles analysis of ET pathways in huge biomolecules. This poster presents our recent results[2] and discusses the roles of the protein environments in mediating long-distance electron tunneling and quantum interference effects among multiple ET pathways. We also discuss its applicability to a non-Condon theory[3] for analyzing the inelastic electron tunneling mechanism in protein, such as a hypothesis of the vibrational theory of olfaction. We acknowledge support from JST, PRESTO Grant Number JPMJPR17G4.

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