Relevance of incoherent light-induced coherences for photosynthetic energy transfer

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The interpretation of oscillatory features in experimental signals from photosynthetic pigment–protein complexes excited by laser pulses [1] has been motivating vigorous interest in quantum effects in photosynthetic energy transfer (ET) [2]. 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 ET should be in terms of a nonequilibrium steady state (NESS) [3], which is formed when a photosynthetic complex is continuously photoexcited and continuously delivers the excitation energy to the reaction center (RC), in which charge separation takes place.

We study ET in a molecular aggregate that is driven by weak incoherent radiation and coupled to its immediate environment and the RC. We combine a second-order treatment of the photoexcitation with an exact treatment of the excitation–environment coupling and formulate the hierarchy of equations of motion (HEOM) that explicitly takes into account the photoexcitation process [4]. We develop an efficient numerical scheme that respects the continuity equation for the excitation fluxes to compute the NESS of the aggregate [5]. The NESS is most conveniently described in the so-called preferred basis, in which the excitonic density matrix is diagonal. The preferred basis, which is analogous to the set of normal modes of a system of coupled harmonic oscillators, is singled out by the interplay between excitation generaton, energy relaxation, dephasing, and excitation delivery to the RC. Having established the proper NESS description, we are in position to critically reassess the involvement of stationary coherences in the photosynthetic ET and claims that stationary coherences may enhance the ET efficiency. Focusing on a model photosynthetic dimer, we examine the properties of the NESS. In the limit of slow delivery to the RC, we find that the NESS is quite similar to the excited-state equilibrium in which the stationary coherences originate from the excitation–environment entanglement. When the excitation delivery is slower than energy relaxation processes, we establish a general relationship between the NESS picture and time-dependent description of an incoherently driven, but unloaded system.

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