

Non-Hermitian Approach for Modeling of Noise-Assisted Quantum Electron Transfer in Photosynthetic Complexes

Gennady P. Berman, T-4;
Alan R. Bishop, PADSTE;
Alexander I. Nesterov,
Universidad de Guadalajara

Nature has evolved photosynthetic organisms to be extremely complex bio-engines that capture visible light in their peripheral light-harvesting complexes (LHC) and transfer excited-state energy (as excitons) through the proximal LHC of photosystem II (PSII) and photosystem I (PSI) to the reaction centers (RC). The primary charge separation occurs in the RC (which works as a battery), leading to the formation of an electrochemical gradient. During the past two decades, crystallographic structures for many photosynthetic complexes (PC), including the LHCs and RCs, have been determined to a resolution of 2.5–3 Å. PCs operate in a thermal protein environment at ambient temperature and in the presence of external “classical” sources of noise. In spite of this, recent experiments based on 2D laser-pulse femtosecond photon-echo spectroscopy revealed a long-lived exciton-electron quantum coherence in PCs such as the Fenna-Matthews-Oslov (FMO) and marine algae. This occurs mainly because the dynamics of the electron transfer (ET) are so rapid (a few) that the thermal fluctuations and external noise are unable to significantly destroy quantum coherence. Consequently, the exciton/electron dynamics in LHCs-RCs must be described using quantum-mechanical methods.

An important consequence of the exciton/electron dynamics in LHCs-RCs is the high ET efficiency of the peripheral antennae complexes (close to 100%). Usually two different approaches are used to describe the influence of the protein environment on the ET. One is based on the thermal protein environment. In this case, the environment acts self-consistently on the electron system and, in combination with the transition amplitudes between sites and pigments, provides the ET rates between the sites and the Gibbs equilibrium state for the LHC-RC subsystem. The second approach is based on considering an external classical noise provided by the protein vibrations. This approach results in a transfer rate for the electron, but does not lead to Gibbs equilibrium states. The choice of approach depends on the specific experimental situation that the theoretical model is intended to describe.

We model the quantum ET in the photosynthetic RC, using a non-Hermitian Hamiltonian approach. Our model includes: (1) two protein cofactors, donor and acceptor, with discrete energy levels; and (2) a third protein pigment (sink), which has a continuous energy spectrum. Interactions are introduced between the donor and acceptor, and between the acceptor and the sink, with noise acting between the donor and acceptor. The noise is considered classically (as an external random force) and it is described by an ensemble of two-level systems (random fluctuators). Each fluctuator has two independent parameters, amplitude and switching rate. We represent the noise by a set of fluctuators with

fitting parameters (boundaries of switching rates), which allows us to build a desired spectral density of noise in a wide range of frequencies. We analyze the quantum dynamics and the efficiency of the ET as a function of: (1) the energy gap between the donor and acceptor, (2) the strength of the interaction with the continuum, and (3) noise parameters. As an example, numerical results are presented for the ET through the active pathway in a quinone-type photosystem II RC. As demonstrated in Fig. 1, the donor, $|d\rangle$, interacts with the acceptor, $|a\rangle$, through the corresponding matrix element, V_{da} . The third protein pigment, RC (sink), has a continuous energy spectrum, and is described by two parameters: (1) its density of states, $\rho(E)$, and (2) its strength of interaction with the acceptor, V_{aj} . The sink is described self-consistently, by using the Feshbach projection method on the “donor-acceptor” intrinsic states, within a non-Hermitian Hamiltonian approach [1]. We apply our results to the quantum dynamics of the electron transfer in the active branch of the quinone-type PSII reaction center. The collective external noise produced by the environment of the proteins acts on the donor-acceptor sub-system. Usually, the presence of noise acts as an incoherent pump in the system under consideration. But, as our results demonstrate, the simultaneous influence of both noise and the sink significantly assist, under appropriate conditions, the quantum efficiency of the electron transfer. We derived the expression for the electron transfer rate, which describes the tunneling to the sink, in the presence of noise. We calculate explicitly the corresponding region of parameters of the

noise-assisted quantum-electron transfer for sharp and flat redox potentials and for noise described by an ensemble of two-level fluctuators. Our results show that even in this simplified model, the quantum dynamics of the electron transfer to the sink can be rather complicated, and sensitive to many parameters. Further analytical research and numerical simulations are required to extend our approach for: (1) complicated dependencies of the density of states on energy in the sinks for flat and sharp redox potentials in the presence of noise and thermal environments and (2) more complicated LHCs-RCs complexes. The problem of the electron transfer optimization also requires further analysis.

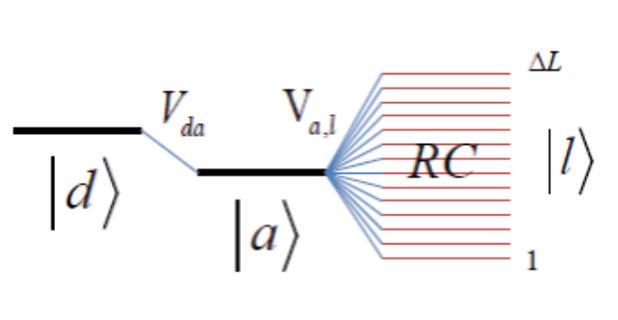


Fig. 1. A reaction center consisting of the donor and acceptor discrete energy levels, with the acceptor coupled to a sink with a continuous spectrum.