

Theoretical Studies of Chemical Dynamics in Condensed and Biomolecular Systems

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Photosynthesis provides the energy source for essentially all living things on Earth, and its functionality has been one of the most fascinating mysteries of life. Photosynthetic conversion of the energy of sunlight into its chemical form suitable for cellular processes involves a variety of physicochemical mechanisms. The conversion starts with the absorption of a photon of sunlight by one of the light-harvesting pigments, followed by transfer of electronic excitation energy to the reaction center, where charge separation is initiated. At low light intensities, surprisingly, the quantum efficiency of the transfer is near unity. A longstanding question in photosynthesis has been the following: *How does light harvesting deliver such high efficiency in the presence of disordered and fluctuating dissipative environments? Why does not energy get lost?* At high light intensities, on the other hand, the reaction center is protected by regulation mechanisms that lead to quenching of excess excitation energy in light harvesting proteins. The precise mechanisms of these initial steps of photosynthesis are not yet fully elucidated from the standpoint of molecular science.

1. Electronic Excitation Transfer Dynamics in Light Harvesting Systems

Recently, the technique of two-dimensional electronic spectroscopy has been applied to explore photosynthetic light harvesting complexes. The observation of long-lived quantum superposition or coherence between eigenstates of electronic excitations (excitons) in a pigment-protein complex stimulated a huge burst of activity among experimentalists and theorists. Much of the interest arose because the finding of electronic

quantum coherence is a “warm, wet, and noisy” biological system was considered very surprising. The initial experiments were carried out at 77 K, but more recent studies have detected coherence lasting at least 300 fs at physiological temperatures. These observations have led to the suggestion that electronic quantum coherence might play a role in achieving the remarkable efficiency of photosynthetic light harvesting. At the same time, the observations have raised questions regarding the role of the surrounding protein in protecting the coherence. In order to elucidate origins of the long-lived electronic coherence and its interplay with the protein environment, we have investigated appropriate theoretical frameworks and concepts with the use of statistical mechanics¹⁾ and in cooperation with experiment.²⁾

In particular, we have discussed significance of the finite timescale site-dependent reorganization dynamics of the protein environment surrounding (bacterio)chlorophyll molecules. The electronic coupling $\hbar J$ between pigments and the excitation-environment coupling characterized by the reorganization energy $\hbar\lambda$ are two fundamental interaction mechanisms determining the nature of electronic energy transfer (EET) in photosynthetic complexes. Ordinarily, photosynthetic EET is discussed only in terms of the mutual relation between magnitudes of the two couplings, as just described. However, the nature of EET also depends on the mutual relation between two timescales, the characteristic timescale of the environmental reorganization, τ (Figure 1), and the inverse of the electronic coupling, J^{-1} , that is the time the excitation needs to move from one pigment to another neglecting any additional perturbations. We showed that even in the region of reorganization energy much larger than that of a typical situation of photosynthetic light harvesting the sluggish reorganization

dynamics allows the excitation to stay above an energy barrier separating two local minima, which correspond to the two sites in the adiabatic potential surface, for a prolonged time (Figure 2). This is an essential origin of the experimentally observed long-lived electronic coherence.

Further, we showed this energy barrier is much small in comparison with the thermal energy $k_B T$ (almost activation-less) in the parameter regime corresponding to natural light harvesting systems. It can be considered that natural photosynthetic light harvesting systems avoid local trapping of electronic excitations, which yields a situation that electronic excitation energy gets lost in the presence of disordered and fluctuating dissipative environments. By extending this argument, we are now tackling the above questions regarding the remarkable quantum efficiency and smart regulation mechanism that photosynthetic light harvesting systems exhibit.

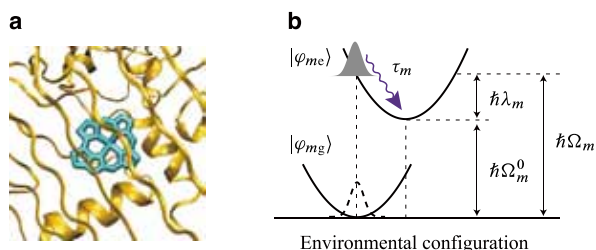


Figure 1. Schematic illustration of the m th pigment embedded in a protein (a) and the electronic ground and excited states of the m th pigment, $|\varphi_{mg}\rangle$ and $|\varphi_{me}\rangle$, affected by nuclear motion of the protein environment (b). After electronic excitation in accordance with the vertical Franck-Condon transition, reorganization takes place from the equilibrium nuclear configuration with respect to the electronic ground state $|\varphi_{mg}\rangle$ to the actual equilibrium configuration in the excited state $|\varphi_{me}\rangle$ with dissipation of the reorganization energy, $\hbar\lambda_m$. This reorganization of the protein environment proceeds on a characteristic timescale, τ_m .

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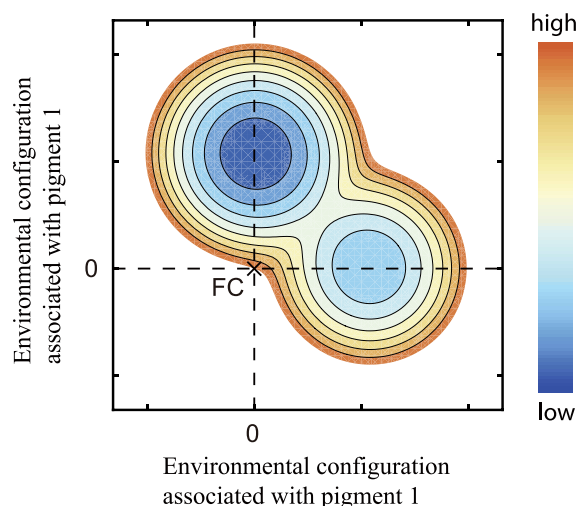


Figure 2. Schematic illustration of adiabatic excitonic potential surface of coupled two pigments. The point of origin corresponds to the Franck-Condon state. The energy of the point is higher than the barrier between the minima; therefore, we find that the electronic excited state is delocalized just after the excitation. As time increases, the dissipation of reorganization energy proceeds and the excitation will fall off into one of the minima and become localized. Namely, sluggish dissipation of reorganization energy increases the time an electronic excitation stays above an energy barrier separating pigments and thus prolongs delocalization over the pigments.

References

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