

Theoretical Studies of Chemical Dynamics in Condensed and Biomolecular Systems

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Education

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Professional Employment

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2008 JPSP Postdoctoral Fellow for Research Abroad, University of California, Berkeley

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Awards

2015 10th Condensed-Matter Science Prize, Japan

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Keywords

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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. Particularly, recent observations of long-lived beating phenomena in two-dimensional electronic spectra of photosynthetic pigment-protein complexes stimulated a huge burst of activity in an interdisciplinary community of molecular science and quantum physics.

Selected Publications

- A. Ishizaki and Y. Tanimura, "Quantum Dynamics of System Strongly Coupled to Low-Temperature Colored Noise Bath: Reduced Hierarchy Equations Approach," *J. Phys. Soc. Jpn.* **74**, 3131–3134 (2005).
- A. Ishizaki and G. R. Fleming, "Unified Treatment of Quantum Coherent and Incoherent Hopping Dynamics in Electronic Energy Transfer: Reduced Hierarchy Equation Approach," *J. Chem. Phys.* **130**, 234111 (10 pages) (2009).
- A. Ishizaki and G. R. Fleming, "Theoretical Examination of Quantum Coherence in a Photosynthetic System at Physiological Temperature," *Proc. Natl. Acad. Sci. U.S.A.* **106**, 17255–17260 (2009).
- A. Ishizaki, T. R. Calhoun, G. S. Schlau-Cohen and G. R. Fleming, "Quantum Coherence and Its Interplay with Protein Environments in Photosynthetic Energy Transfer," *Phys. Chem. Chem. Phys.* **12**, 7319 (2010). [Invited perspective article]
- A. Ishizaki and G. R. Fleming, "Quantum Coherence in Photosynthetic Light Harvesting," *Annu. Rev. Condens. Matter Phys.* **3**, 333–361 (2012). [Invited review article]
- Y. Fujihashi, G. R. Fleming and A. Ishizaki, "Impact of Environmentally Induced Fluctuations on Quantum Mechanically Mixed Electronic and Vibrational Pigment States in Photosynthetic Energy Transfer and 2D Electronic Spectra," *J. Chem. Phys.* **142**, 212403 (12 pages) (2015).

1. Influences of Quantum Mechanically Mixed Electronic and Vibrational Pigment States in 2D Electronic Spectra of Photosynthetic Systems: Strong Electronic Coupling Cases

In 2D electronic spectroscopy studies, long-lived quantum beats have recently been observed in photosynthetic systems, and several theoretical studies have suggested that the beats are produced by quantum mechanically mixed electronic and vibrational states. Concerning the electronic-vibrational quantum mixtures, the impact of protein-induced fluctuations was examined by calculating the 2D electronic spectra of a weakly coupled dimer with the Franck-Condon active vibrational modes in the resonant condition [Fujihashi *et al.*, *J. Chem. Phys.* **142**, 212403 (2015)]. This analysis demonstrated that quantum mixtures of the vibronic resonance are rather robust under the influence of the fluctuations at cryogenic temperatures, whereas the mixtures are eradicated by the fluctuations at physiological temperatures. However, this conclusion cannot be generalized because the magnitude of the coupling inducing the quantum mixtures is proportional to the inter-pigment electronic coupling. In this study, we explore the impact of the fluctuations on electronic-vibrational quantum mixtures in a strongly coupled dimer with an off-resonant vibrational mode. Toward this end, we calculate energy transfer dynamics and 2D electronic spectra of a model dimer that corresponds to the most strongly coupled bacteriochlorophyll molecules in the Fenna-Matthews-Olson complex in a numerically accurate manner. The quantum mixtures are found to be robust under the exposure of protein-induced fluctuations at cryogenic temperatures, irrespective of the resonance. At 300 K, however, the quantum mixing is disturbed more strongly by the fluctuations, and therefore, the beats in the 2D spectra become obscure even in a strongly coupled dimer with a resonant vibrational mode. Further, the overall behaviors of the energy transfer dynamics are demonstrated to be dominated by the environment and coupling between the 0–0 vibronic transitions as long as the Huang-Rhys factor of the vibrational mode is small. The electronic-vibrational quantum mixtures do not necessarily play a significant role in electronic energy transfer dynamics despite contributing to the enhancement of long-lived quantum beating in the 2D spectra.¹⁾

2. Fluctuations in Electronic Energy Affecting Singlet Fission Dynamics and Mixing with Charge Transfer State: Quantum Dynamics Study

Singlet fission is a spin-allowed process by which a singlet excited state is converted to two triplet states. To understand

mechanisms of the ultrafast fission via a charge transfer (CT) state, one has investigated the dynamics through quantum-dynamical calculations with the uncorrelated fluctuation model; however, the electronic states are expected to experience the same fluctuations induced by the surrounding molecules because the electronic structure of the triplet pair state is similar to that of the singlet state except for the spin configuration. Therefore, the fluctuations in the electronic energies could be correlated, and the 1D reaction coordinate model may adequately describe the fission dynamics. In this work we develop a model for describing the fission dynamics to explain the experimentally observed behaviors. We also explore impacts of fluctuations in the energy of the CT state on the fission dynamics and the mixing with the CT state. The overall behavior of the dynamics is insensitive to values of the reorganization energy associated with the transition from the singlet state to the CT state, although the coherent oscillation is affected by the fluctuations. This result indicates that the mixing with the CT state is rather robust under the fluctuations in the energy of the CT state as well as the high-lying CT state.²⁾

3. A Variational Master Equation Approach to Quantum Dynamics with Off-Diagonal Coupling in a Sub-Ohmic Environment

A master equation approach based on an optimized polaron transformation is adopted for dynamics simulation with simultaneous diagonal and off-diagonal spin–boson coupling. Two types of bath spectral density functions are considered, the Ohmic and the sub-Ohmic. The off-diagonal coupling leads asymptotically to a thermal equilibrium with a nonzero population difference $P_z(t \rightarrow \infty) \neq 0$, which implies localization of the system, and it also plays a role in restraining coherent dynamics for the sub-Ohmic case. Since the new method can extend to the stronger coupling regime, we can investigate the coherent–incoherent transition in the sub-Ohmic environment. Relevant phase diagrams are obtained for different temperatures. It is found that the sub-Ohmic environment allows coherent dynamics at a higher temperature than the Ohmic environment.³⁾

References

- 1) Y. Fujihashi, G. R. Fleming and A. Ishizaki, *J. Chin. Chem. Soc.* **63**, 49–56 (2016).
- 2) Y. Fujihashi and A. Ishizaki, *J. Phys. Chem. Lett.* **7**, 363–369 (2016).
- 3) K.-W. Sun, Y. Fujihashi, A. Ishizaki and Y. Zhao, *J. Chem. Phys.* **144**, 204106 (8 pages) (2016).

Awards

ISHIZAKI, Akihito; 10th Condensed-Matter Science Prize, Japan (2015).

ISHIZAKI, Akihito; 10th Young Scientist Award of the Physical Society of Japan (2016).