Theoretical Studies of Chemical Dynamics in Condensed and Biomolecular Systems

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Education
2001 B.S. Kyoto University
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Professional Employment
2006 JSPS Research Fellow, Kyoto University
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2016 Professor, Institute for Molecular Science
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Awards
2015 10th Condensed-Matter Science Prize, Japan
2015 10th Young Scientist Award of the Physical Society of Japan
2016 18th Sir Martin Wood Prize
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Quantum dynamic phenomena are ubiquitous in molecular processes, and yet remain a challenge for experimental and theoretical investigations. On the experimental side, it has become possible to explore molecules on a time scale down to a few femtoseconds. This progress in ultrafast spectroscopy has opened up real-time observation of dynamic processes in complex chemical and biological systems and has provided a strong impetus to theoretical studies of condensed phase quantum dynamics.

Essentially, any quantum systems can never be regarded as "isolated systems." Quantum systems are always in contact with "the outside world," and hence their quantum natures are sometimes sustained and sometimes destroyed. In condensed phase molecular systems, especially, quantum systems are affected by the huge amount of dynamic degrees of freedom such as solvent molecules, amino acid residues in proteins, and so forth. Balance between robustness and fragility of the quantum natures may dramatically alter behaviors of chemical dynamics and spectroscopic signals. Therefore, theoretical tools to adequately describe (1) dynamical behaviors of quantum systems affected by the huge amount of dynamic degrees of freedom and (2) the interaction with radiation fields should be developed.

For this purpose, our research group has been tackling the following subjects:

(1) Developments of condensed phase quantum dynamic theories
(2) Quantum theories to describe dynamical and transport processes in materials and biological systems
(3) Theoretical investigations on measurement and control with the use of atomic-molecular-optical (AMO) physics approaches.

In recent years, specifically, special attention is devoted to the subject (3). We have been examining whether ideas and concepts in the field of quantum science and technology would provide novel control knobs that supplement classical parameters in conventional spectroscopic tools such as frequencies and time delays.

Selected Publications

- A. Ishizaki and G. R. Fleming, "Quantum Coherence in Photosynthetic Light Harvesting," *Annu. Rev. Condens. Matter Phys.* **3**, 333–361 (2012). [Invited review article]
- G. D. Scholes *et al.*, "Using Coherence to Enhance Function in Chemical and Biophysical Systems," *Nature* **543**, 647–656 (2017).
- T. P. Nguyen and A. Ishizaki, "Control of Excitation Energy Transfer in Condensed Phase Molecular Systems by Floquet Engineering," *J. Phys. Chem. Lett.* **9**, 1243 (2018).
- A. Kato and A. Ishizaki, "Non-Markovian Quantum-Classical Ratchet for Ultrafast Long-Range Electron–Hole Separation in Condensed Phases," *Phys. Rev. Lett.* **121**, 647 (2018).
- Y. Fujihashi, R. Shimizu and A. Ishizaki, "Generation of Pseudo-Sunlight via Quantum Entangled Photons and the Interaction with Molecules," *Phys. Rev. Res.* **2**, 023256 (2020).
- A. Ishizaki, "Probing Excited-State Dynamics with Quantum Entangled Photons: Correspondence to Coherent Multidimensional Spectroscopy," *J. Chem. Phys.* **153**, 051102 (2020). [Editor's Pick]

1. Dynamics of a Quantum System Interacting with White Non-Gaussian Baths: Poisson Noise Master Equation

Quantum systems are unavoidably open to their surrounding degrees of freedom. The theory of open quantum systems is thus crucial to understanding the fluctuations, dissipation, and decoherence of a quantum system of interest. Typically, the bath is modeled as an ensemble of harmonic oscillators, which yields Gaussian statistics of the bath influence on the quantum systems. However, there are also phenomena in which the bath consists of two-state systems, spins, or anharmonic oscillators; therefore, the non-Gaussian properties of the bath become important. Nevertheless, a theoretical framework to describe quantum systems under the influence of such non-Gaussian baths is not well established. Here, we develop a theory to describe quantum dissipative systems affected by Poisson noise properties of the bath, because the Lévi-Itô decomposition theorem asserts that Poisson noise is fundamental in describing arbitrary white noise beyond Gaussian properties. We introduce a quantum bath model that allows for the consistent description of dissipative quantum systems. The obtained master equation reveals non-Gaussian bath effects in the white noise regime, and provides an essential step toward describing open quantum dynamics under the influence of generic baths.[1)]

2. Pathway Selectivity in Time-Resolved Spectroscopy Using Two-Photon Coincidence Counting with Quantum Entangled Photons

Ultrafast optical spectroscopy is a powerful technique for studying the dynamic processes of molecular systems in condensed phases. However, in molecular systems containing many dye molecules, the spectra can become crowded and difficult to interpret owing to the presence of multiple nonlinear optical contributions. In this work, we theoretically propose time-resolved spectroscopy based on the coincidence counting of two entangled photons generated via parametric down-conversion with a monochromatic laser. We demonstrate that the use of two-photon counting detection of entangled photon pairs enables the selective elimination of the excited-state absorption signal. This selective elimination cannot be realized with classical coherent light. We anticipate that the proposed spectroscopy will help simplify the spectral interpretation of complex molecular and material systems comprising multiple molecules.[2)]

3. A Coarse-Grained Description of Anharmonic Lattice Environments Affecting the Quantum Dynamics of Charge Carriers

Lattice softness has a significant impact on charge carrier dynamics in condensed matter systems. Examples include the remarkable carrier lifetimes and defect tolerances of hybrid organic-inorganic perovskites. Recent studies suggest the contribution of quartic anharmonicity of the lattice vibrations. The quartic anharmonicity can be discussed with a double-well potential, and the transition between the two minima can be coarse-grained as a two-state jump stochastic process. Such a stochastic approach is typically employed to describe fluctuations introduced into a system by two-state transitions in the surroundings. To investigate charge transport in materials, however, it is crucial to describe not only the fluctuations but also the dynamic lattice distortion associated with charge transport. Therefore, there is a need for a theory to describe the charge carrier dynamics proceeding alongside the lattice distortion dynamics. In this study, we present a theory that describes quantum dynamics under the influence of an environment with two stable states, termed a bistable environment. The theory describes the effects of fluctuations and dissipation induced from the bistable environment in a reasonable manner, and the effects exhibit a different temperature dependence than the widely employed Gaussian environment. The physical implication of this temperature dependence is provided in terms of the environmental dynamics. The results of this study are expected to provide a step forward in describing charge carrier dynamics in materials with lattice softness and pronounced lattice anharmonicity.[3)]

4. Network Analysis with Quantum Dynamics Clarifies Why Photosystem II Exploits both Chlorophyll *a* and *b*

In land plants, chlorophyll-*a* and chlorophyll-*b* in light-harvesting proteins are responsible for absorbing solar energy. While the individual characteristics of these pigments are well-understood, the advantages of their coexistence have not been fully elucidated. Here, we presented a principled framework based on complex network analysis and quantum dynamics to investigate and quantify the features of this coexistence during excitation energy transfer in a photosystem II supercomplex. By using model networks with diverse chlorophyll compositions, our analysis revealed that the excited energy preferentially flows through specific domains, where excessive energy can be controlled, solely in those supercomplexes with a natural chlorophyll-*a*/*b* ratio, resulting in a moderate charge separation yield. Our findings suggested that light-harvesting proteins with the natural chlorophyll-*a*/*b* ratio are optimized to safely and efficiently capture light energy across various light intensities. By leveraging our framework, we could gain valuable insights into the mechanisms by which light-harvesting proteins harvest light energy and adapt to changing environmental conditions.[4)]

References

1) K. Funo and A. Ishizaki, *Phys. Rev. Lett.* **132**, 170402 (2024).
2) Y. Fujihashi, A. Ishizaki and R. Shimizu, *J. Chem. Phys.* **160**, 104201 (2024).
3) K. Miwa, S. Sakamoto, K. Funo and A. Ishizaki, submitted.
4) E. Kim, D. Lee, S. Sakamoto, J.-Y. Jo, M. Vargas, A. Ishizaki, J. Minagawa and H. Kim, submitted.