

Theoretical Studies of Chemical Dynamics in Condensed and Biomolecular Systems

Department of Theoretical and Computational Molecular Science
Division of Theoretical Molecular Science II



ISHIZAKI, Akihito
Professor
[ishizaki@ims.ac.jp]

Education

2008 D.S. Kyoto University

Professional Employment

2006 JPSP Research Fellow, Kyoto University

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

2010 Postdoctoral Fellow, Lawrence Berkeley National Laboratory

2012 Research Associate Professor, Institute for Molecular Science

2013 Fellow 2012–2013, Wissenschaftskolleg zu Berlin

2016 Professor, Institute for Molecular Science

Professor, The Graduate University for Advanced Studies

Visiting professor, Nagoya University

Awards

2015 10th Condensed-Matter Science Prize, Japan

2016 10th Young Scientist Award of the Physical Society of Japan

2016 18th Sir Martin Wood Prize

2017 The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology
The Young Scientists' Prize

Member

Assistant Professor
NGUYEN, Thanh Phuc

Post-Doctoral Fellow
KATO, Akihito
FUJIHASHI, Yuta
IKEDA, Tatsushi

Secretary
AKABA, Atsuko

Keywords

Quantum Dissipative Systems in Complex Molecular Systems, Quantum Optics, Light-Matter Interaction

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, 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]
- 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).
- Y. Fujihashi, M. Higashi and A. Ishizaki, “Intramolecular Vibrations Complement the Robustness of Primary Charge Separation in a Dimer Model of the Photosystem II Reaction Center,” *J. Phys. Chem. Lett.* **9**, 4921 (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).

1. Quantum Dynamics Investigation on Chiral-Induced Spin Selectivity in Helical Molecules

Charge transfer processes in DNA have attracted considerable attention over several decades in relation with its possible role to the long-range oxidative damage of DNA. In recent years, however, a new dimension has been brought to this research field. Naaman and coworkers revealed that electrons transmitted through a double-stranded DNA molecule exhibited a preferred spin polarization at room temperature [*Science* **331**, 894 (2011)]. Similar effects were found in various chiral molecules. This effect is currently referred to as chirality induced spin selectivity. Such organic helical molecules are non-magnetic; nevertheless, they can serve as highly efficient spin filters. In this regard, chiral molecules are expected to open a new avenue in molecular spintronics.

In this work, we developed a theoretical framework to investigate quantum dynamics of spinful electrons in a helical molecule under the influence of both the spin-orbit interaction and the surrounding environment. In the literature, the Landauer theory has offered a way to calculate spin-dependent charge current under the assumption that electrons propagated freely across a conductor. Therefore, we focused on the quantum master equation approach. Furthermore, the geometric phase associated with the spin-orbit interaction has been analyzed, and it has been revealed that impacts of the phase upon the spin dynamics depends on individual paths.¹⁾

2. Generation of Pseudo-Sunlight via Quantum Entangled Photon Pairs and the Interaction with Molecular Systems

Light incident upon molecules trigger fundamental processes in diverse systems present in nature. However, under natural conditions such as sunlight illumination, it is impossible to assign known times for photon arrival owing to continuous pumping, and therefore, the photo-induced processes cannot be easily investigated. In time-resolved optical spectroscopy, in contrast, investigations on the processes can be conducted by synchronizing the initial excitations in the entire ensemble with pulsed laser and thereby amplifying the microscopic dynamics in a constructively interferential fashion. Hence, whether dynamics initiated by sunlight irradiation might be different from those detected with laser spectroscopy is still being debated.

In this work, we addressed quantum entangled photon pairs generated with the parametric down-conversion (PDC) in birefringent crystals. The photon number statistics obeys the geometric distribution rather than the Poisson distribution, and therefore, the entangled photons are expected to reproduce characteristics of the sunlight photons. Furthermore, it became possible to investigate photo-induced dynamical processes with quantitative underpinnings, because expressions of quantum states of the pseudo-sunlight photons can be theoretically obtained. We showed that the average photon number of the sunlight in a specific frequency spectrum, e.g., the visible light, can be reconstructed by adjusting the PDC crystal length and pump frequency, and thereby molecular dynamics induced by

the pseudo-sunlight can be investigated. The entanglement time, which is the hallmark of quantum entangled photons, can serve as a control knob to resolve the photon arrival times under the pseudo-sunlight irradiation, enabling investigations on real-time dynamics triggered by the pseudo-sunlight photons.²⁾

3. Control of Quantum Dynamics of Electronic Excitation Transfer in Molecular Loop Structures: Spontaneous Breaking of Chiral Symmetry

Manipulation of quantum systems is the basis for many promising quantum technologies. However, how quantum mechanical principles can be used to manipulate the dynamics of quantum dissipative systems remains unanswered because of strong decoherence effects arising from interaction with the surrounding environment. In this work, we demonstrate that electron transfer dynamics in molecular loop structures can be manipulated with the use of Floquet engineering by applying a laser field. Despite strong dephasing, the system's dynamics spontaneously breaks the chiral symmetry of the loop in a controllable fashion, followed by the generation of a robust steady-state electronic current without an external voltage. An exponential scaling law that relates the magnitude of the current to the system-environment coupling strength is revealed numerically. The breaking of chiral symmetry and the consequent controllable unidirectional flow of electrons could be employed to construct functional molecular electronic circuits.³⁾

4. Precise Determination of Excitation Energies in Condensed-Phase Molecular Systems Based on Exciton-Polariton Measurements

The precise determination of the excitation energies in condensed-phase molecular systems is important for understanding system-environment interactions as well as for the prerequisite input data of theoretical models used to study the dynamics of the system. The excitation energies are usually determined by fitting of the measured optical spectra that contain broad and unresolved peaks as a result of the thermally random dynamics of the environment. Herein, we propose a method for precise energy determination by strongly coupling the molecular system to an optical cavity and measuring the energy of the resulting polariton. The effect of thermal fluctuations induced by the environment on the polariton is also investigated, from which a power scaling law relating the polariton's linewidth to the number of molecules is obtained. The power exponent gives important information about the environmental dynamics.⁴⁾

References

- 1) A. Kato, T. Ikeda and A. Ishizaki, in preparation.
- 2) Y. Fujihashi, R. Shimizu and A. Ishizaki, submitted.
- 3) T. P. Nguyen and A. Ishizaki, *Phys. Rev. B* **99**, 064301 (2019).
- 4) T. P. Nguyen and A. Ishizaki, *Phys. Rev. Research* **1**, 033019 (2019).