RESEARCH ACTIVITIES

Theoretical and Computational Molecular Science

The goal of the Department is understanding and prediction of static and dynamic properties, reactions, and functions in condensed phase including biomolecular and heterogeneous catalytic systems by developing novel theories and computational methodologies based on theories in quantum mechanics, statistical mechanics, and solid state physics. The Department collaborates with Research Center for Computational Science on researches.

Theoretical Studies of Reactions, Functions, and Fluctuations in Many-Body Molecular Systems

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

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Education
1988 B.S. Keio University
1990 M.E. Kyoto University
1995 Ph.D. The Graduate University for Advanced Studies

Professional Employment
1990 Technical staff, Institute for Molecular Science
1994 Research Associate, Nagoya University
1998 Associate Professor, Nagoya University
2005 Professor, Institute for Molecular Science
2006 Professor, The Graduate University for Advanced Studies

Member
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MORI, Toshifumi*
KODA, Shin-ichi
JSPS Post-Doctoral Fellow
MATSUMURA, Yoshihiro
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CHIBA, Fumika

Keywords Reactions, Functions, Fluctuations

Many-body molecular systems, such as (supercooled) liquids and biomolecules, exhibit complex fluctuations. Furthermore, in these systems, various physical properties and biological functions are created and chemical reactions proceed under the fluctuations. We aim to elucidate the properties, functions, and reactions by investigating fluctuations and dynamics of the many-body molecular systems.

We have investigated fluctuations and dynamics of liquids by developing computational method for multi-dimensional nonlinear spectroscopy that can reveal detailed dynamical infomation not available from conventional linear spectroscopy. Consequently, we revealed the molecular origins of the ultrafast energy relaxation and time evolution of inhomogeneous fluctuations in liquid water. In supercooled liquids, rare and non-uniform structural changes, called dynamic heterogeneity, are induced by fluctuations. We elucidated the relationship between the lifetime of the dynamic heterogeneity and the fragility using the three-time correlation function of density fluctuations.

We study the molecular origin of anomalous properties of liquid water. We revealed that the anomalies of liquid water are related to the structural and dynamical instabilities hidden in the experimentally inaccessible region and the physical reason of the low glass transition of liquid water. Now we investigate how rare but persistent structural relaxations proceed at low temperatures towards the glass transition temperature.

Complex conformational fluctuations and changes are also found in biomolecular systems. In addition, the conformational dynamics are considered to be essential for biological functions. We examine the relationship between fluctuation and biomolecular function found in the robust circadian rhythm of the clock protein KaiC and the efficient excitation energy transfer in photosynthetic systems. We investigate dynamic effects of enzymatic reactions, and find the importance of prearranged states for the rare but persistent enzymatic reactions. Furthermore, we examine dynamic disorder in conformational changes of proteins at the molecular level.

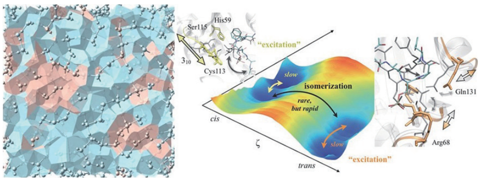

Figure 1. Snapshot of two-state model in supercooled water consisting of high- and low-density liquids (left) and schematic of 2D free energy surface for enzymatic reaction (right).

Selected Publications

- T. Yagasaki and S. Saito, *Annu. Rev. Phys. Chem.* **64**, 55–75 (2013). T. L. C. Jansen, S. Saito, J. Jeon and M. Cho, *J. Chem. Phys.* **150**, 100901 (17 pages) (2019), C. R. Baiz *et al.*, *Chem. Rev.* **120**, 7152–7218 (2020).
- K. Kim and S. Saito, *J. Chem. Phys. (Special Topic on Glass Transition)* **138**, 12A506 (12 pages) (2013).
- S. Saito, B. Bagchi and I. Ohmine, *J. Chem. Phys.* **149**, 124504 (8 pages) (2018), S. Saito and B. Bagchi, *J. Chem. Phys.* **150**, 054502 (14 pages) (2019).
- T. Mori and S. Saito, *J. Phys. Chem. Lett.* **10**, 474–480 (2019).
- S. Saito, M. Higashi and G. R. Fleming, *J. Phys. Chem. B* **123**, 9762–9772 (2019).

1. Molecular Mechanism of Acceleration and Retardation of Collective Orientation Relaxation of Water Molecules in Aqueous Solutions$^{1)}$

The collective orientation relaxation (COR) of water molecules in aqueous solutions is faster or slower with an increase in the concentration of the solutions than that in pure water; for example, acceleration (deceleration) of the COR is observed in a solution of sodium chloride (tetramethyl ammonium chloride) with increasing concentration. However, the molecular mechanism of the solution and concentration dependence of the relaxation time of the COR has not yet been clarified. We theoretically investigate the concentration dependence of the COR of water molecules in solutions of tetramethylammonium chloride (TMACl), guanidinium chloride (GdmCl), and sodium chloride (NaCl). Based on the Mori–Zwanzig equation, we identify two opposing factors that determine the COR of water molecules in any aqueous solution: The correlation of dipole moments and the single-molecule orientation relaxation. We reveal the molecular mechanism of the concentration dependence of the relaxation time of the COR in the TMACl, GdmCl, and NaCl solutions in terms of these two factors.

2. Effects of Interfaces on Structure and Dynamics of Water Droplets on a Graphene Surface: A Molecular Dynamics Study$^{2)}$

The structure and dynamics of water droplets on a bilayer graphene surface are investigated using molecular dynamics simulations. The effects of solid/water and air/water interfaces on the local structure of water droplets are analyzed in terms of the hydrogen bond distribution and tetrahedral order parameter. It is found that the local structure in the core region of a water droplet is similar to that in liquid water. On the other hand, the local structure of water molecules at the solid/water and air/water interfaces, referred to as the interface and surface regions, respectively, consists mainly of three-coordinated molecules that are greatly distorted from a tetrahedral structure. This study reveals that the dynamics in different regions of the water droplets affects the intermolecular vibrational density of states: It is found that in the surface and interface regions, the intensity of vibrational density of states at ~50 cm^{-1} is enhanced, whereas those at ~200 and ~500 cm^{-1} are weakened and redshifted. These changes are attributed to the increase in the number of molecules having fewer hydrogen bonds in the interface and surface regions. Both single-molecule and collective orientation relaxations are also examined. Single-molecule orientation relaxation is found to be marginally slower than that in liquid water. On the other hand, the collective orientation relaxation of water droplets is found to be significantly faster than that of liquid water because of the destructive correlation of dipole moments in the droplets. The negative correlation between distinct dipole moments also yields a blue-shifted libration peak in the absorption spectrum. It is also found that the water–graphene interaction affects the structure and dynamics of the water droplets, such as the local water structure, collective orientation relaxation, and the correlation between dipole moments. This study reveals that the water/solid and water/air interfaces strongly affect the structure and intermolecular dynamics of water droplets and suggests that the intermolecular dynamics, such as energy relaxation dynamics, in other systems with interfaces are different from those in liquid water.

3. Microscopic Insights into Dynamic Disorder in the Isomerization Dynamics of the Protein BPTI$^{3)}$

Understanding the dynamic disorder behind a process, *i.e.*, the dynamic effect of fluctuations that occur on a timescale slower or comparable with the timescale of the process, is essential for elucidating the dynamics and kinetics of complicated molecular processes in biomolecules and liquids. Despite numerous theoretical studies of single-molecule kinetics, our microscopic understanding of dynamic disorder remains limited. In the present study, we investigate the microscopic aspects of dynamic disorder in the isomerization dynamics of the Cys14–Cys38 disulfide bond in the protein bovine pancreatic trypsin inhibitor, which has been observed by nuclear magnetic resonance. We use a theoretical model with a stochastic transition rate coefficient, which is calculated from the 1-ms-long time molecular dynamics trajectory obtained by Shaw *et al*. [*Science* **330**, 341–346 (2010)]. The isomerization dynamics are expressed by the transitions between coarse-grained states consisting of internal states, *i.e.*, conformational sub-states. In this description, the rate for the transition from the coarse-grained states is stochastically modulated due to fluctuations between internal states. We examine the survival probability for the conformational transitions from a coarse-grained state using a theoretical model, which is a good approximation to the directly calculated survival probability. The dynamic disorder changes from a slow modulation limit to a fast modulation limit depending on the aspects of the coarse-grained states. Our analysis of the rate modulations behind the survival probability, in relation to the fluctuations between internal states, reveals the microscopic origin of dynamic disorder.

References

1) N. Moritsugu, T. Nara, S.-i. Koda, K. Tominaga and S. Saito, *J. Phys. Chem. B* **124**, 11730–11737 (2020).

2) M. Manish, A. K. Metya, J. K. Singh and S. Saito, *J. Chem. Phys.* **154**, 164704 (12 pages) (2021).

3) Y. Matsumura and S. Saito, *J. Chem. Phys.* **154**, 224113 (11 pages) (2021).

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Theoretical Studies on Novel Physical Properties Arising from Many-Body Interaction

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Education

2005	B.S. Osaka University
2010	Ph.D. Osaka University

Professional Employment

2010	Postdoctoral Fellow, Osaka University
2011	Special Postdoctral Researcher, RIKEN
2013	Assistant Professor, The University of Tokyo
2015	Lecturer, The University of Tokyo
2019	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies

Awards

2008	L'Oréal–UNESCO Japan National Fellowships for Women in Science
2011	Best Poster Award in ISSS-6 Internal Symposium on Surface Science
2017	Young Scientist Award of the Physical Society of Japan
2019	The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology The Young Scientists' Prize
2020	The 1st Award for Early Career Women Scientists of the Japan Society of Vacuum and Surface Science
2021	The 2nd Fumiko Yonezawa Memorial Prize of the Physical Society of Japan

Member

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Keywords Quantum Many-Body Interaction, Density Functional Theory, Quantum Field Theory

Quantum many-body interaction is a source of novel physical properties in the condensed matters. In our group, we develop theoretical methods by combining quantum field theory and density functional theory, and carry out collaborative research with experimental groups. As specific targets, we focus on magnetism in nanostructure and energy dissipation.

For magnetism in nanostructure, we are interested in the Kondo effect and spin–orbit interaction. The Kondo effect arises from the interaction between the localized spin and conduction electrons, which forms a characteristic many-body state so called the Kondo singlet state. The spin–orbit interaction originating from relativistic effect constrains the direction of magnetic moment to specific direction. We investigate the possibility of novel physical phenomena induced by these interactions in the nanostructure and molecules on surfaces.

For energy dissipation, we focus on the effect of electron–phonon interaction. The electron–phonon interaction is one of the most fundamental interactions in the condensed matter physics, and the quantitative evaluation in realistic materials is highly demanding. We adopt the ab-initio calculation to analyze the signal of electron–phonon coupling in surface spectroscopy and thermal properties in various kind of solids.

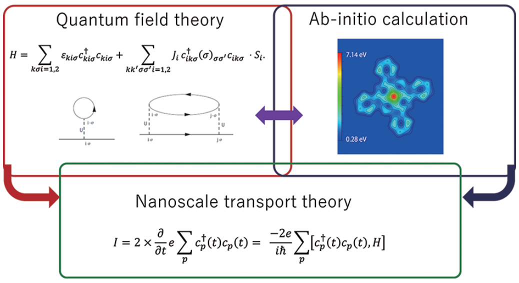

Figure 1. Schematic image of the theoretical method developed in our group.

Selected Publications

- E. Minamitani, N. Tsukahara, D. Matsunaka, Y. Kim, N. Takagi and M. Kawai, "Symmetry-Driven Novel Kondo Effect in a Molecule," *Phys. Rev. Lett.* **109**, 086602 (2012).
- E. Minamitani, R. Arafune, N. Tsukahara, Y. Ohda, S. Watanabe, M. Kawai, H. Ueba and N. Takagi, "Surface Phonon Excitation on Clean Metal Surfaces in Scanning Tunneling Microscopy," *Phys. Rev. B* **93**, 085411 (2016).
- E. Minamitani, N. Takagi and S. Watanabe, "Model Hamiltonian Approach to the Magnetic Anisotropy of Iron Phthalocyanine at Solid Surfaces," *Phys. Rev. B* **94**, 205402 (2016).
- R. Hiraoka, E. Minamitani, R. Arafune, N. Tsukahara, S. Watanabe, M. Kawai and N. Takagi, "Single-Molecule Quantum Dot as a Kondo Simulator," *Nat. Commun.* **8**, 16012 (2017).
- E. Minamitani, R. Arafune, T. Frederiksen, T. Suzuki, S. M. F. Shahed, T. Kobayashi, N. Endo, H. Fukidome, S. Watanabe and T. Komeda, "Atomic-Scale Characterization of the Interfacial Phonon in Graphene/SiC," *Phys. Rev. B* **96**, 155431 (2017).
- E. Minamitani, M. Ogura and S. Watanabe, "Simulating Lattice Thermal Conductivity in Semiconducting Materials Using High-Dimensional Neural Network Potential," *Appl. Phys. Express* **12**, 095001 (2019).

1. Ab Initio Investigation for Initial Process of Joule Heating in Semiconductor

Joule heating in semiconductors is a fundamental problem in solid-state physics. The resulting thermal damage, reduction in operational reliability, and power consumption of nanoscale transistors have become increasingly critical as the device size decreases. The macroscopic definition of the Joule heating is the dot product of the electric field and the current density. The microscopic process of Joule heating in a steady state is described as the energy balance between the electron and phonon intermediated by electron–electron, electron–impurity, electron–phonon, and phonon–phonon interactions under nonequilibrium conditions in the presence of a high electric field. Until recently, the empirical treatment of the band structure and the electron–phonon coupling prevents us from understanding the detail of relaxation process induced by these scattering process quantitatively and microscopically.

We propose a methodology for quantitative investigation of the energy relaxation process with the ab initio treatment of electronic states and electron–phonon interactions by approximating the nonequilibrium electron distribution function as being in equilibrium with an effective temperature.1) This approximation is known as the two-temperature model because the electrons and phonons are described by different effective temperatures, the electron temperature (T_e) and lattice temperature (T_l). The two-temperature model becomes reasonable if the electron equilibration time is sufficiently shorter than the time required for energy relaxation from electrons to phonons. Under such conditions, the Joule heating process can be described by the following three steps: First, electrons accelerated by an electric field are scattered elastically by electron–electron and electron–impurity interactions with a short relaxation time. This process randomizes the electron energy and momentum, and consequently, the electron distribution becomes isotropic in **k**-space, which can be described by a Fermi distribution with T_e. Second, the inelastic electron–phonon scattering with a longer energy relaxation time occurs, and the energy is transferred from the hot electrons to the cold phonons specified by T_l. Finally, the excited phonons are thermalized by the slow phonon–phonon interaction, and the heat energy is radiated to the environment or transported to a thermal bath such as a substrate and/or electrode by thermal phonons. We focus on the second energy transfer process as the initial step of Joule heating and develop a method to evaluate this process based on ab initio calculations.

Recent progress in ab initio calculations by combining density functional theory and the Wannier interpolation technique has enabled the evaluation of electron–phonon coupling with high precision. This technique has been employed to evaluate the transport properties of semiconducting materials. Here, we combine the ab initio calculation of the transport properties with the two-temperature concept. We applied this theoretical approach to bulk Si as a specific target.

As result, we found that the microscopic initial process of Joule heating differed in the electron and hole carriers. Figures 2 (a)–(d) show the phonon dispersion and decomposition of the energy relaxation rates into the contributions from the phonons with <27 meV, <50 meV, and >50 meV energy at low and high T_l as functions of E. The contributions from the phonons with medium energy, the LA and TO modes at the zone boundary, differ for the electron and hole carriers. For the electron carriers, there is a substantial contribution from medium-energy phonons at both low and high T_l. In particular, the relaxation via medium-energy phonons is dominant at low E at low T_l. In contrast, for the hole carriers, the contribution from medium-energy phonons is minor compared to that from the TO and zone center LO modes, except at a very low E at a low T_l. The origin of the differences can be attributed to the presence/absence of the intervalley scattering process and the isotropic/anisotropic band structures in the electron and hole carriers. The important factors that govern the energy relaxation process can be controlled by strain. A detailed ab initio investigation of the energy relaxation rate in a strained structure remains a topic for future research.

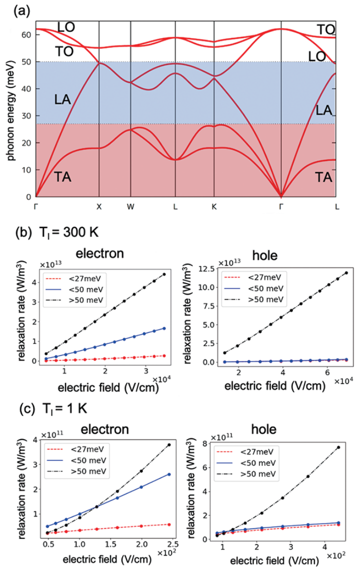

Figure 2. (a) Phonon band structure of bulk Si. The energy relaxation rates of electron and hole carriers are decomposed into contributions from phonons in the three energy ranges at (b) T_l = 300 K and (c) T_l = 1 K.

2. Other Ongoing Projects:

- Thermal Properties in Amorphous Solids

Reference

1) E. Minamitani, *Phys. Rev. B* **104**, 085202 (2021).

Awards

MINAMITANI, Emi; The 1st Award for Early Career Women Scientists of the Japan Society of Vacuum and Surface Science (2020).
MINAMITANI, Emi; The 2nd Fumiko Yonezawa Memorial Prize of the Physical Society of Japan (2021).
SHITADE, Atsuo; 15th Young Scientist Award of the Physical Society of Japan (2021).
MIWA, Kuniyuki; 15th Young Scientist Award of the Physical Society of Japan (2021).

Theoretical Studies of Chemical Dynamics in Condensed and Biomolecular Systems

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Education

2001	B.S. Kyoto University
2005	M.S. Kyoto University
2008	D.S. Kyoto University

Professional Employment

2006	JSPS Research Fellow, Kyoto University
2008	JSPS 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
2020	JSPS Prize
2020	Japan Academy Medal

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SAKAMOTO, Souichi
JO, Ju-Yeon
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 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. Probing Excited-State Dynamics with Quantum Entangled Photons

Quantum light is a key resource for promoting quantum technology. One such class of technology aims to improve the precision of optical measurements using engineered quantum states of light. In this study, we investigate transmission measurement of frequency-entangled broadband photon pairs generated via parametric down-conversion with a monochromatic laser. It is observed that state-to-state dynamics in the system under study are temporally resolved by adjusting the path difference between the entangled twin beams when the entanglement time is sufficiently short. The non-classical photon correlation enables time-resolved spectroscopy with monochromatic pumping. It was further demonstrated that the signal corresponds to the spectral information along anti-diagonal lines of, for example, two-dimensional Fourier-transformed photon echo spectra. This correspondence inspires us to anticipate that more elaborately engineered photon states would broaden the availability of quantum light spectroscopy.1)

2. Achieving Two-Dimensional Optical Spectroscopy with Temporal and Spectral Resolution Using Quantum Entangled Three Photons

Recent advances in techniques for generating quantum light have stimulated research on novel spectroscopic measurements using quantum entangled photons. One such spectroscopy technique utilizes non-classical correlations among entangled photons to enable measurements with enhanced sensitivity and selectivity. In this work, we investigated spectroscopic measurement utilizing entangled three photons generated through cascaded parametric down-conversion. In this measurement, time-resolved entangled photon spectroscopy with monochromatic pumping [A. Ishizaki, *J. Chem. Phys.* **153**, 051102 (2020)] is integrated with the frequency-dispersed two-photon counting technique, which suppresses undesired accidental photon counts in the detector and thus allows one to separate the weak desired signal. This time-resolved frequency-dispersed two-photon counting signal, which is a function of two frequencies, is shown to provide the same information as that of coherent two-dimensional optical spectra. The spectral distribution of the phase-matching function works as a frequency filter to selectively resolve a specific region of the two-dimensional spectra, whereas the excited-state dynamics under investigation are temporally resolved in the time region longer than the entanglement time. The signal is not subject to Fourier limitations on the joint temporal and spectral resolution, and therefore, it is expected to be useful for investigating complex molecular systems in which multiple electronic states are present within a narrow energy range.2)

3. Insights into Photosynthetic Energy Transfer Gained from Free-Energy Structure: Coherent Transport, Incoherent Hopping, and Vibrational Assistance Revisited

Giant strides in ultrashort laser pulse technology have enabled real-time observation of dynamical processes in complex molecular systems. Specifically, the discovery of oscillatory transients in the two-dimensional electronic spectra of photosynthetic systems [G. S. Engel, *et al.*, *Nature* **446**, 782 (2007)] stimulated a number of theoretical investigations exploring the possible physical mechanisms of the remarkable quantum efficiency of light harvesting processes. In this work, we revisited the elementary aspects of environment-induced fluctuations in the involved electronic energies and present a simple way to understand energy flow with the intuitive picture of relaxation in a funnel-type free-energy landscape. The presented free-energy description of energy transfer reveals that typical photosynthetic systems operate in an almost barrierless regime. The approach also provides insights into the distinction between coherent and incoherent energy transfer and the criteria by which the necessity of the vibrational assistance is considered.3)

4. Direct and Ultrafast Probing of Quantum Many-Body Interaction and Mott-Insulator Transition through Coherent Two-Dimensional Spectroscopy

Interactions between particles in quantum many-body systems play a crucial role in determining the electric, magnetic, optical, and thermal properties of the system. The recent progress in the laser-pulse technique has enabled the manipulations and measurements of physical properties on ultrafast timescales. In this work, we proposed a method for the direct and ultrafast probing of quantum many-body interaction through coherent two-dimensional (2D) spectroscopy. Up to a moderate interaction strength, the inter-particle interaction manifests itself in the emergence of off-diagonal peaks in the 2D spectrum before all the peaks coalesce into a single diagonal peak as the system approaches the Mott-insulating phase in the strongly interacting regime. The evolution of the 2D spectrum as a function of the time delay between the second and third laser pulses can provide important information on the ultrafast time variation of the interaction.4)

References

1) A. Ishizaki, *J. Chem. Phys.* **153**, 051102 (7 pages) (2020). [Editor's Pick]
2) F. Fujihashi and A. Ishizaki, *J. Chem. Phys.* **155**, 044101 (13 pages) (2021).
3) A. Ishizaki and G. R. Fleming, *J. Phys. Chem. B* **125**, 3286–3295 (2021).
4) T. P. Nguyen and Q. T. Pham, *arXiv:*2009.08598 (2021).

Awards

FUJIHASHI, Yuta; 15th Young Scientist Award of the Physical Society of Japan (2021).
ISHIZAKI, Akihito; Research Award of Quantum Life Science Society (2021).

Theoretical Studies of Functional Molecular Systems and Heterogeneous Catalysts

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Education

1988	B.E. Kyoto University
1990	M.E. Kyoto University
1993	Ph.D. Kyoto University

Professional Employment

1993	Postdctral Fellow, Institute for Fundamental Chemistry
1994	JSPS Postdoctoral Fellow
1994	Visiting Researcher, Heidelberg University (–1995)
1995	Assistant Professor, Kyoto University
2002	Associate Professor, Kyoto University
2006	Theoretical Research Division Supervisor, Kyoto University (–2008)
2008	Professor, Institute for Molecular Science Professor, The Graduate University for Advanced Studies
2012	Professor, Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University (additional post)

Awards

2009	APATCC Pople Medal
2009	QSCP Prize CMOA

Member
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ZHAO, Pei
KANAZAWA, Yuki
Graduate Student
SAKUMA, Koya
HATORI, Atsuya
Secretary
SUGIMOTO, Yukari

Keywords Quantum Chemistry, Photophysical Chemistry, Heterogeneous Catalysis

We develop the accurate electronic structure theories and investigate the photochemistry and catalysis theoretically. Currently, our focuses are following research subjects.

(1) Coupled cluster theory for excited states of large system

We develop the coupled cluster theories and their efficient computational algorithm aiming at large-scale calculations of molecular excited states. We also develop the basic theories and methodologies that are useful for fundamental chemistry and applied chemistry; for example, PCM SAC-CI method for effectively describing the solvent effects on excited states, CAP/SAC-CI method for locating metastable resonance states, general-R method for multiple excited states, and active-space method for efficiently describing complex electronic states.

(2) Heterogeneous catalysis

Metal nanoclusters supported by metal oxides or polymers achieve highly efficient catalytic reactions. We study the catalytic activity of these complex systems by means of quantum chemical calculations and informatics theories. We have elucidated the importance of the perimeter sites at heterojunction of Ag nanocluster supported by alumina surface in terms of H_2 activation, the mechanism of methanol oxidation on Au:PVP and the unique coupling reactions on Au/Pd:PVP. We proceed these works in the project of Elements Strategy Initiative for Catalysts and Batteries (ESICB).

(3) Photophysical chemistry

Our accurate electronic structure theories are applied to wide varieties of theoretical studies and sometimes in cooperation with experiments on the photophysical properties and excited-state dynamics of nano-bio systems like photo-electronic devices, photofunctional molecules, and biosensors. Target molecules include nanocarbons like fullerenes, near-IR absorbing phthalocyanine congeners, dye-sensitized solar cells, organometallic compounds for artificial photosynthesis, biological chemosensors, and bio-imaging probes.

(4) Theoretical spectroscopy

New quantum states, single-site and two-site double-core hole states, have been observed owing to the recent development of free electron laser and coincidence spectroscopy. We have proposed new chemical concept regarding the physical properties or relaxation processes of these quantum states in cooperation with experiments. We also perform accurate theoretical analysis for the state-of-the-art molecular spectroscopy; for example, the electronic transitions in the FUV region by ATR-FUV spectroscopy and the excited-state relaxation processes by pump–probe spectroscopy.

Selected Publications

- R. Cammi, R. Fukuda, M. Ehara and H. Nakatsuji, "SAC-CI Method in the Polarizable Continuum Model-Theory for Solvent Effect on Electronic Excitation of Molecules in Solution," *J. Chem. Phys.* **133**, 024104 (24 pages) (2010).
- N. Berrah, M. Tashiro, M. Ehara *et al.*, "Double Core-Hole Spectroscopy for Chemical Analysis with an Intense X-Ray Femtosecond Laser," *Proc. Natl. Acad. Sci. U.S.A.* **108**, 16912–16915 (2011).
- M. Ehara and T. Sommerfeld, "CAP/SAC-CI Method for Calculating Resonance States of Metastable Anions," *Chem. Phys. Lett.* **537**, 107–112 (2012).
- P. Hirunsit, K. Shimizu, R. Fukuda, S. Namuangruk, Y. Morikawa and M. Ehara, "Cooperative H_2 Activation at Ag Cluster/θ-Al_2O_3 Dual Perimeter Sites: A DFT Study," *J. Phys. Chem. C* **118**, 7996–8006 (2014).

1. Mechanistic Studies on Photoinduced Catalytic Olefin Migration Reactions at the Pd(II) Centers of a Porous Crystal, Metal-Macrocycle Framework[1)]

Porous crystals with well-defined active metal centers on the pore surface have high potential as heterogeneous metal catalysts. We have recently demonstrated that a porous molecular crystal, metal-macrocycle framework (MMF), catalyzes olefin migration reactions by photoactivation of its $Pd^{II}Cl_2$ moieties exposed on the crystalline channel surface. Herein we report a mechanistic study of the photoinduced olefin migration reactions at the Pd^{II} active centers of MMF. Several experiments, including a deuterium scrambling study, revealed that olefin migration is catalyzed *via* an alkyl mechanism by *in situ* generated Pd-H species on the channel surface during photoirradiation. This proposed mechanism was further supported by DFT and ONIOM calculations.

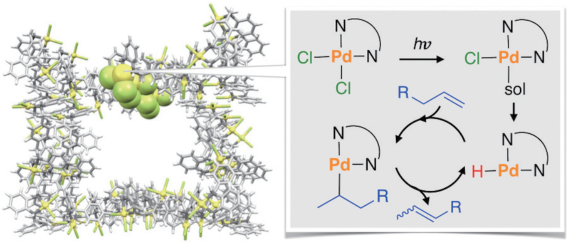

Figure 1. Porous Crystal Metal-Macrocyclic Framework show characteristic photoinduced olefin migration reaction at the Pd^{II} active centers.

2. Selective Catalytic Reduction of NO with NH_3 over Cu-Exchanged CHA, GME, and AFX Zeolites: A Density Functional Theory Study[2)]

Density functional theory calculations have been applied to study the selective catalytic reduction of NO by NH_3 over the Cu-exchanged zeolites with *cha*, *gme*, and *aft* cages. The Cu^I, Cu^{II}, and $[Cu^{II}(OH)]^+$ ions are considered as the active sites to study both the reduction and oxidation processes during the catalytic cycle. In the case of the reduction process, the NH_2NO formation at the $[Cu^{II}(OH)]^+$ site possesses high barriers in the three frameworks, while the lower barriers are found at the Cu^{II} site. Importantly, it is found that the barriers are largely decreased at the solvated $[Cu^{II}(NH_3)_4]^{2+}$ site for the *cha* and *aft* frameworks, while the barrier is only slightly decreased for the *gme* cage. As for the oxidation, the nitrate formation has similar reaction barriers at the Cu^I site of the three frameworks, which are lower than the following nitrite formation. In particular, the smallest *gme* cage possesses the highest barrier for the nitrite formation. Calculations on the O_2 activation by the NH_3-solvated Cu dimer revealed that the *cha* and *aft* cages have better performance than the *gme* cage, and the much smaller adsorption energy of O_2 in the *gme* cage indicates the unfavorable O_2 insertion. Therefore, the selectivity caused by the cage size is identified during the reaction process, and the *cha* and *aft* cages are more favorable.

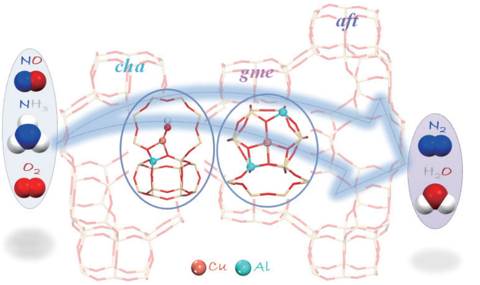

Figure 2. Density functional theory calculations on selective catalytic reduction of NO by NH_3 over the Cu-exchanged zeolites with *cha*, *gme*, and *aft* cages revealed the selectivity caused by the cage size during the reaction process.

3. Facet-Dependent Catalytic Activity of Anatase TiO_2 for the Selective Catalytic Reduction of NO with NH_3: A Dispersion-Corrected Density Functional Theory Study[3)]

Recently, the facet-dependent catalytic activity of anatase TiO_2 for the selective catalytic reduction of NO with NH_3 (NH_3-SCR) has been observed experimentally. In this study, the NH_3-SCR of NO on the TiO_2 (001) and (101) surfaces was systematically investigated using dispersion-corrected density functional theory. We propose that the surface-assisted mechanism is predominant on the (001) surface, which involves the oxygen active sites playing a crucial role in facilitating the reaction. The NH_3 dissociation step reveals the largest activation energy barrier (E_a) of 61 kJ/mol on the (001) surface, whereas the NH_2NO decomposition step has the largest barrier, $E_a \approx 156$ kJ/mol, on the (101) surface. The results obtained by calculation are consistent with the experimental results, which have shown that a TiO_2 nanosheet with a dominant (001) facet shows superior catalytic performance in NH_3-SCR of NO compared to TiO_2 nanoparticles with dominant (101) facet.

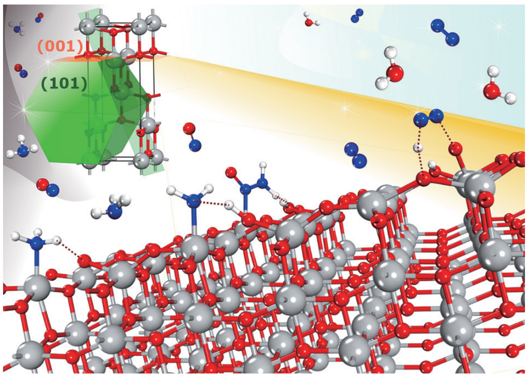

Figure 3. NH_3-SCR of NO on the (001) facet of anatase TiO_2.

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Molecular Dynamics Simulations of Disease-Related Biomolecules

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Keywords Molecular Dynamics Simulation, Protein, Amyloid

Biomolecules such as proteins and peptides have complicated free-energy landscape with many local minima. The conventional canonical-ensemble molecular dynamics (MD) simulations tend to get trapped in a few of the local-minimum states. To overcome these difficulties, we have proposed new generalized-ensemble algorithms, such as replica-permutation method. We apply these methods to proteins and peptides and try to predict the native structures of proteins as in Figure 1.

We are also interested in disease-related biomolecules. For example, protein aggregates such as spherical substances called oligomers and acicular substances called amyloid fibrils (Figure 2) cause more than 30 kinds of diseases. Alzheimer's disease is thought to be caused by aggregated amyloid-β (Aβ) peptides. To overcome these diseases, it is essential to understand the aggregate genesis and disruption of Aβ peptides. We perform such MD simulations of oligomers and amyloid fibrils.

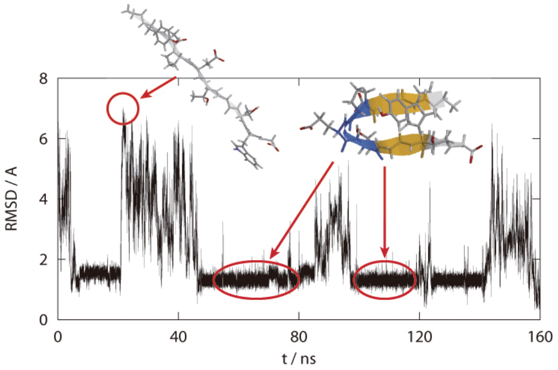

Figure 1. Time series of protein folding simulation.

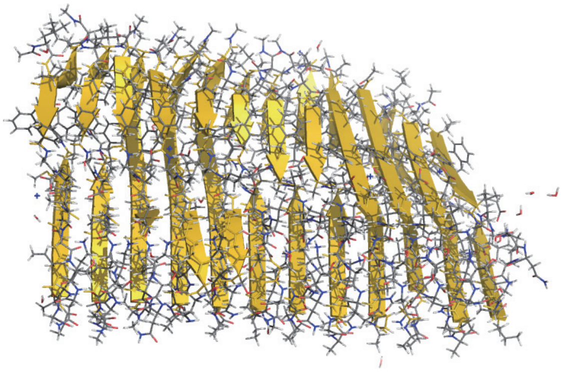

Figure 2. Snapshot of an Aβ amyloid fibril.

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- S. G. Itoh and H. Okumura, "Replica-Permutation Method with the Suwa-Todo Algorithm beyond the Replica-Exchange Method," *J. Chem. Theory Comput.* **9**, 570–581 (2013).
- S. G. Itoh and H. Okumura, "Oligomer Formation of Amyloid-β(29-42) from Its Monomers Using the Hamiltonian Replica-Permutation Molecular Dynamics Simulation," *J. Phys. Chem. B* **120**, 6555–6561 (2016).

1. Role of Water Molecules in the Laser-Induced Disruption of Amyloid Fibrils Observed by Nonequilibrium Molecular Dynamics Simulations

Water plays a crucial role in the formation and destruction of biomolecular structures. The mechanism for destroying biomolecular structures was thought to be an active breaking of hydrogen bonds by water molecules. However, using nonequilibrium molecular dynamics simulations, in which an Aβ amyloid fibril was destroyed via infrared free-electron laser (IR-FEL) irradiation, we discovered a new mechanism, in which water molecules disrupt protein aggregates,1) as shown in Figure 3. The intermolecular hydrogen bonds formed by C=O and N–H in the fibril are broken at each pulse of laser irradiation. These bonds usually spontaneously reform after the irradiation in many cases. However, when a water molecule happens to enter the gap between C=O and N–H, it inhibits the reformation of the hydrogen bonds. Such sites become defects in the regularly aligned hydrogen bonds, from which all hydrogen bonds in the intermolecular β-sheet are broken as the fraying spreads. This role of water molecules is entirely different from other known mechanisms. This new mechanism can explain the recent experiments showing that the amyloid fibrils are not destroyed by laser irradiation under dry conditions. Additionally, we found that helix structures form more after the amyloid disruption; this is because the resonance frequency is different in a helix structure. Our findings provide a theoretical basis for the application of IR-FEL to the future treatment of amyloidosis.

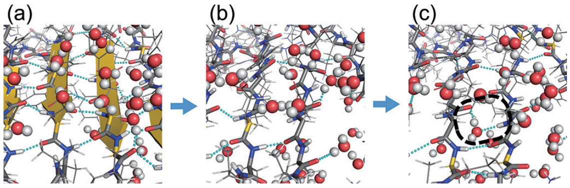

Figure 3. Snapshots of the disruption process of the hydrogen bonds between the Aβ peptides. (a) Hydrogen bonds are formed between Aβ peptides. (b) These hydrogen bonds are broken by the IR-FEL. (c) Water molecule enters the gap between C=O and N–H, it inhibits the reformation of the hydrogen bonds.

2. Replica-Permutation Molecular Dynamics Simulations of an Amyloid-β(16–22) Peptide and Polyphenols

Polyphenols are known to inhibit the aggregation of Aβ peptides. We performed all-atom replica-permutation molecular dynamics simulations of an Aβ fragment, $A\beta_{16–22}$, and two kinds of polyphenols, myricetin and rosmarinic acid in explicit water solvent.2) We found that glutamic acid E22 of the $A\beta_{16–22}$ peptide has the highest probability to bind to the polyphenols and specified the hydroxyl groups and carboxyl groups of polyphenols that contribute to the binding.

3. "Bucket Brigade" Using Lysine Residues in RNA-Dependent RNA Polymerase of SARS-CoV-2

The RNA-dependent RNA polymerase (RdRp) of severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2) is a promising drug target for coronavirus disease 2019 (COVID-19) because it plays the most important role in the replication of the RNA genome. Nucleotide analogs such as remdesivir and favipiravir are thought to interfere with the RNA replication by RdRp. More specifically, they are expected to compete with nucleoside triphosphates, such as adenosine triphosphate (ATP). However, the process in which these drug candidates and nucleoside triphosphates are taken up by RdRp remains unknown. We performed all-atom molecular dynamics simulations to clarify the recognition mechanism of RdRp for these drug candidates and ATP that were at a distance.3) The ligand recognition ability of RdRp decreased in the order of remdesivir, favipiravir, and ATP. We also identified six recognition paths. Three of them were commonly found in all ligands, and the remaining three paths were ligand-dependent ones. In the common two paths, it was observed that the multiple lysine residues of RdRp carried the ligands to the binding site like a "bucket brigade," as shown in Figure 4. In the remaining common path, the ligands directly reached the binding site. Our findings contribute to the understanding of the efficient ligand recognition by RdRp at the atomic level.

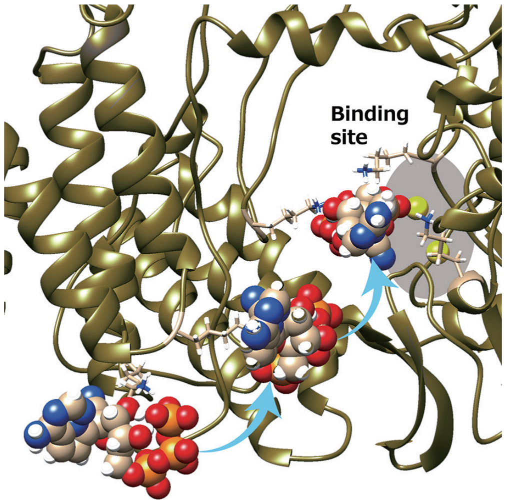

Figure 4. Remdesivir (shown in the sphere model) is transferred to two Mg^{2+} ions (yellow-green spheres) at the binding site of the RNA polymerase while being passed from one lysine residue (shown in the stick model) to another.

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Functional Dynamics of Biomolecular Machines Revealed by Theoretical Methods

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Keywords Theoretical Biophysics, Biomolecular Machines, Molecular Motors

Biomolecular machines, such as molecular motors and transporters in the cell, are known to change their structure when they function. For example, ATP synthase, which synthesizes ATP in mitochondria, is a molecular motor that uses chemical energy to rotate. Transporters, which transport substrate molecules across the cell membrane, perform substrate transport by changing their structure between an inwardly and outwardly open structure relative to the membrane. Our goal is to elucidate the mechanism of these elaborate and dynamic nanomachines created by nature at the atomic and molecular level, and to control their functions based on our findings.

We would like to understand the mechanism of biomolecular machines by "seeing" the motion of biomolecular machines at the moment they function, on a computer at the molecular level. However, this is not an easy task, because biomolecular machines are huge molecules, and their functioning time scale is slow (for a molecular scale) at milliseconds or longer. Conventional atomistic molecular dynamics (MD) simulations cannot cover millisecond-long functional dynamics, especially for a large system like typical biomolecular machines. Therefore, we are trying to capture the motion at the moment of function by using methods such as an importance sampling technique, or coarse-graining multiple atoms together.

We have been working on biomolecular motors such as ATP synthase. ATP synthase is a rotary motor that produces most of ATP required in the cell. It is composed of two rotary motors: F_o and F_1. F_o motor is embedded in the membrane driven by proton gradient, while F_1 motor is driven by ATP hydrolysis reaction. We clarified how the rotation of F_1 motor is driven by a key chemical step, P_i release after ATP hydrolysis reaction, by accelerating atomistic MD simulations with external forces.

Transporters are membrane proteins that transport their substrates across the membrane. We have studied Na^+/H^+ antiporter that exchanges sodium ions and protons inside and outside the cell. The ion transport by the Na^+/H^+ antiporter was simulated in atomic detail with the transition path sampling technique to capture the moment of the ion transports. The simulations predicted the mutation that can speed up the ion transport. The mutation was tested in experiments and shown to speed up the ion transport twice faster than the wild type. Therefore, we succeeded in controlling the function of the transporter based on mechanism obtained from simulations.

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- K. Okazaki and G. Hummer, "Elasticity, Friction, and Pathway of γ-Subunit Rotation in F_oF_1-ATP Synthase," *Proc. Natl. Acad. Sci. U.S.A.* **112**, 10720–10725 (2015).
- K. Okazaki, D. Wöhlert, J. Warnau, H. Jung, Ö. Yildiz, W. Kühlbrandt and G. Hummer, "Mechanism of the Electroneutral Sodium/Proton Antiporter PaNhaP from Transition-Path Shooting," *Nat. Commun.* **10**, 1742 (2019).

1. Mechanism of Unidirectional Motions of Chitinase

Processive cellulase and chitinase recently have been cast new light as a different type of biomolecular motors that use hydrolysis energy of polysaccharides for their unidirectional movements. We used single-molecule trajectories to estimate an underlying diffusion model with chemical-state-dependent free energy profile.[1)] To consider nonequilibrium trajectories driven by the chemical energy consumed by biomolecular motors, we developed a novel framework based on a hidden Markov model, wherein switching among multiple energy profiles occurs reflecting the chemical state changes in motors. The chemical-state-dependent free energy profile underlying the burnt-bridge Brownian ratchet mechanism of processive chitinase was determined.[1)]

2. Mechanism of Na^+/H^+ Antiporter and Engineering of a Faster Transporter

Na^+/H^+ antiporters control pH and Na^+ concentration in the cell by exchanging sodium ions and protons across lipid membranes. They belong to the cation/proton antiporter (CPA) superfamily, and prevail in all domains of life. The archaeal Na^+/H^+ antiporters PaNhaP from *Pyrococcus abyssi* and MjNhaP1 from *Methanocaldococcus jannaschii* as well as human NHE1, which is linked to a wide spectrum of diseases from heart failure to autism and has no structure solved yet, are electroneutral antiporters of the CPA1 family, exchanging one proton against one sodium ion. As a model system in mechanistic studies of electroneutral Na^+/H^+ exchange, we studied the transport mechanism of PaNhaP.[2)]

Na^+/H^+ antiporters use the gradient of either sodium ion or proton to drive the uphill transport of the other ion (Figure 1A). The conformational transition of the transporter makes the ion-binding site accessible from either side of the membrane in the alternating manner. For PaNhaP, the inward-open conformation was obtained by X-ray crystallography, while the outward-open conformation is not known experimentally. We modelled the outward-open conformation by MDFF flexible fitting to the low-resolution outward-open structure of the homologous MjNhaP1 from cryo-EM, followed by the long equilibrium MD simulations. It was shown that the transporter domain moves ~3.5 Å in the direction normal to the membrane to take the outward-open state.

By applying the transition path sampling technique, we sampled unbiased transition paths between the inward- and outward-open states. In analysis of the transition paths, we found hydrophobic gates above and below the ion-binding site, which open and close in response to the domain motions (Figure 1B). From the reaction coordinate analysis, it was shown that open-close motion of the outside gate (Ile163-Tyr255) is a rate-limiting step of the alternating-access conformational change. Based on this result, we weakened the outside gate by mutating the residues to both alanine. It was expected that this mutation lowers the barrier and makes the ion transport faster. It was confirmed by experiments that the ion-transport speed of the mutant is indeed twice faster than the wild-type transporter.

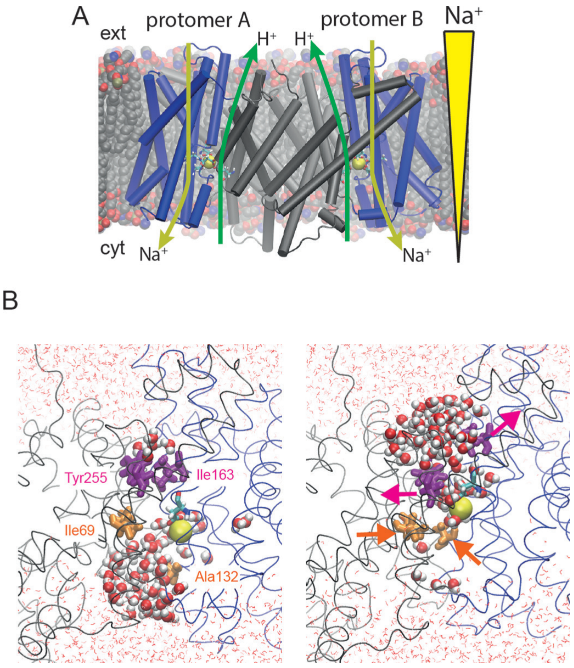

Figure 1. (A) PaNhaP dimer structure. (B) The outside (purple) and inside (orange) gates found in the transition path simulations.

3. Mechanism of Membrane Remodeling by F-BAR Protein Pacsin1

F-Bin/Amphiphysin/Rvs (F-BAR) domain proteins play essential roles in biological processes that involve membrane remodelling, such as endocytosis and exocytosis. Notably, Pacsin1 from the Pacsin/Syndapin subfamily has the ability to transform the membrane into various morphologies: striated tubes, featureless wide and thin tubes, and pearling vesicles. We clarified the membrane curvature induction and sensing characteristics of Pacsin1 by combining all-atom (AA) and coarse-grained (CG) MD simulations.[3)] By matching structural fluctuations between AA and CG simulations, a CG protein model called "Gō-MARTINI" was developed and optimized.[4)] The model should prove useful for describing protein dynamics that are involved in membrane remodeling processes.

References

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4) M. I. Mahmood, A. B. Poma and K. Okazaki, *Front. Mol. Biosci.* **8**, 619381 (2021).

Theoretical Studies on Molecular Aggregates

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Keywords Exciton, Energy and Charge Transfer, Organic Semiconductors

Organic molecules can assemble into an ordered structure by non-covalent interactions, forming various types of aggregates. Molecular aggregates can exhibit remarkable optical and electronic properties that are not observed in isolated molecules. We study optoelectronic properties and quantum dynamics of molecular aggregates. More specifically, we focus on energy and charge transfer dynamics, energy conversions, and structure-property relationship. Our research also include the developments of theoretical and computational methods.

It is still challenging to simulate quantum dynamics of energy or charge transfer in condensed systems. An exciton or electron wave functions can be delocalized over many molecules by intermolecular electronic couplings. By contrast, the wave functions can be localized because of the static disorder and interactions with nuclear degree of freedom. Therefore, successful theoretical descriptions require the inclusions of electronic couplings, static disorder, and electron–phonon or electron–vibration interaction. We develop a method to simulate quantum dynamics in condensed phase by combining molecular dynamics simulations, electronic structure theories, and quantum dynamics methods, as shown in Figure 1. Electronic states of an aggregate are obtained from a large-scale electronic structure calculation, and the model Hamiltonian for an exciton or a charge carrier is derived. The model Hamiltonian is used for simulating energy or charge dynamics by a quantum dynamics method, which incorporates finite-temperature effects and electron–vibration interactions. The combined computational approach allows for bottom-up descriptions of energy or charge transfer dynamics in realistic molecular aggregates.

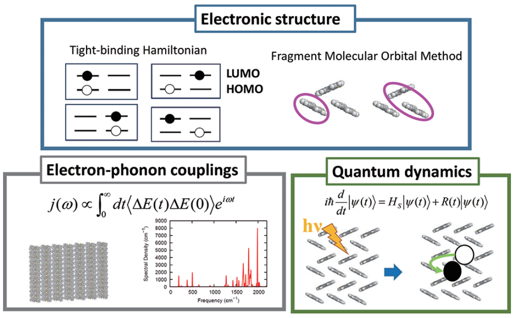

Figure 1. A combine approach to quantum dynamics in molecular aggregates.

We currently investigate electronic states and quantum dynamics at organic interfaces. We also develop the many-body perturbation theory to predict electronic levels at higher accuracy.

Selected Publications

- T. Fujita, S. Atahan-Evrenk, N. P. D. Sawaya and A. Aspuru-Guzik, “Coherent Dynamics of Mixed Frenkel and Charge Transfer Excitons in Dinaphtho[2,3-*b*:2’3’-*f*]thieno[3,2-*b*]-thiophene Thin Films: The Importance of Hole Delocalization,” *J. Phys. Chem. Lett.* 7, 1374–1380 (2016).
- T. Fujita and Y. Mochizuki, “Development of the Fragment Molecular Orbital Method for Calculating Nonlocal Excitations in Large Molecular Systems,” *J. Phys. Chem. A* **122**, 3886–3898 (2018).

1. Fragment-Based Excited-State Calculations Using the GW Approximation and Bethe–Salpeter Equation[1)]

Accurate calculations of electronic states are essential for the computational studies of organic semiconductor materials, toward understanding of electronic processes in organic devices. The electronic processes in organic electronic devices, such as charge injection and electron–hole separation, are governed by the energies of the charged and neutral excited states. Although the Kohn–Sham (KS) density functional theory (DFT) has been established to be accurate for investigating the ground-state properties, a more sophisticated method is required for excited states. The many-body Green's function method within the GW approximation has been established as a standard approach for the first-principle computation of the charged excitations in condensed matter. Further, neutral excited states can be computed using the Bethe–Salpeter equation (BSE) within the GW approximation, *i.e.*, the GW/BSE method. In particular, the GW/BSE method can yield the correct long-range asymptotic behaviors of the charge-transfer excited states in both gas and condensed phases, which is in contrast to the standard time-dependent DFT.

In this study, we present a fragment-based approach for calculating the charged and neutral excited states in molecular systems, based on the many-body Green's function method within the GW approximation and Bethe–Salpeter equation. Our implementation relies on the many-body expansion of the total irreducible polarizability in the basis of fragment molecular orbitals. The GW quasiparticle energies in complex molecular environments are obtained by the GW calculation for the target fragment plus induced polarization contributions of the surrounding fragments at the static Coulomb-hole plus screened exchange level. In addition, we develop a large-scale GW/BSE method for calculating the delocalized excited states of molecular aggregates, based on the fragment molecular orbital method and the exciton model. The accuracy of fragment-based GW and GW/BSE methods were evaluated on the molecular clusters and molecular crystal. We found that the accuracy of the total irreducible polarizability can be improved systematically by including two-body correction terms, and the fragment-based calculations can reasonably reproduce the results of the corresponding unfragmented calculations with a relative error of less than 100 meV. The proposed approach enables the efficient excited-state calculations for large molecular systems with reasonable accuracy.

2. Excited-State Dynamics Based on the FMO and Wavepacket Propagation Method[2)]

We develop a method to investigate the excited-state dynamics in organic molecular aggregates. Our approach is based on three components: (i) FMO-based electronic coupling calculations, (ii) derivations of model Hamiltonians, and (iii) a wavepacket dynamics method. Using the electronic couplings obtained from an FMO calculation for an aggregate, we derive a model Hamiltonian that describes a charge carrier or an exciton in the aggregate. From a theoretical viewpoint, an ab initio many-electron Hamiltonian can be mapped into a reduced one-body or two-body Hamiltonian through the FMO calculation. The time evolution of the model Hamiltonian is then simulated using a wavepacket propagation method. We attempt to understand photophysical and optoelectronic processes in a molecular aggregate as the quasiparticle dynamics described by the model Hamiltonian. We have implemented the electronic coupling calculations and model Hamiltonian derivations into the ABINIT-MP program. In view of computations, an FMO calculation by the ABINIT-MP program provides Hamiltonian matrix elements. The matrix data are then passed to other software that simulates the time propagation.

We investigated the excited-state dynamics in the DNTT thin film and the C_{60}/pentacene (PEN) interface. In particular, we highlight the spatial extents of the electron and hole wave functions that constitute exciton states. We show that the dynamics of the electron and hole wave functions play essential roles in optoelectronic processes, such as the exciton relaxation dynamics and charge separation. Because the extent of delocalization is determined by the interplay among electronic couplings, structural disorder, and finite-temperature effects, the combined approach based on the FMO and wavepacket dynamics is indispensable. Although we have focused on the organic materials, our approach is general and can be applied to other molecular systems. Potential applications include functional supramolecular systems and bio-inspired materials, as well as organic electronic materials.

References

1) T. Fujita and Y. Noguchi, submitted.

2) T. Fujita and T. Hoshi, *Recent Advances of the Fragment Molecular Orbital Method*, Y. Mochizuki, S. Tanaka and K. Fukuzawa, Eds., Springer; Singapore, pp. 547–566. (2021).

Theory and Computation of Reactions and Properties in Solutions and Liquids

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We focus on the projects on ionic liquids (ILs). ILs' projects include both the unique dissolution process of cellulose polysaccharides and the investigation of statical and dynamical properties on ionic liquids.

1. Investigations of Dissolution and Decomposition Mechanisms of a Cellulose Fiber in Ionic Liquids[1] with Molecular Dynamics Simulation

We carried out the studies of dissolution and decomposition mechanisms of cellulose ($I_β$) polymers in ILs. In order to investigate motion of cellulose fibers and intermolecular interactions between cellulose molecules and cationic and anionic species in ILs. We employed the 1-ethyl-3-methylimidazolium acetate IL solvent for target system. From molecular dynamics simulation results, it was found out that the intermolecular interaction energy between cellulose polymers in the IL are reduced, comparing with that in water. Also, our results suggest that the enhancement of the flexibility of rigid cellulose chains triggered by the breakage of intrachain H-bonds due to anions starts decomposition processes accompanied by dissolution processes due to the intercalation of cations, synergistically, and, then, both dissolution and decomposition processes are executed simultaneously.

2. Researches on Statical and Dynamical Properties of Ionic Liquids: Molecular Origin of Low-k Peak of ILs and Dynamical Heterogeneity

We have investigated the molecular level origin of low-k peak (< 0.5 Ang.$^{-1}$) in the structure factor in ILs. In particular, we found out that the structure factor of heterocyclic ring parts in cations largely contribute to low-k peak in ILs. Also, we are going to carry out the study of dynamical properties of ILs, dynamical heterogeneity in ILs at room temperature with molecular dynamics simulation procedure.

Reference

1) T. Ishida, *J. Phys. Chem. B* **124**, 3090–3102 (2020).

Visiting Professors

Visiting Professor

MORI, Hirotoshi *(from Chuo University)*

Electronic Structure Informatics for Designing Functional Liquid Materials

Mixed liquids exhibit various chemical functions depending on their composition and mixing ratio. Contrary to its fundamental scientific importance, however, the chemistry of mixing is an area where molecular level knowledge is not still enough. With the backgrounds, we have been challenging the predictive chemistry of functional liquid materials by developing a novel *ab initio* molecular simulation method with conventional computational cost (Effective fragment potential molecular dynamics; EFP-MD) and a data science approach. In fiscal 2020, we worked on the prediction of Henry's constant values related to the absorption of various industrial exhaust gases for non-aqueous mixed solutions (mixed ionic liquids, ionic liquids/organic solvent mixtures) which supports environmental chemical engineers shortly. We will proceed with our research aiming at the construction of statistical thermodynamic theory for real systems that predict mixed thermodynamics.

Visiting Professor

YANASE, Youichi *(from Kyoto University)*

Theoretical Study of Exotic Quantum Phases

We are working on theoretical studies of exotic quantum phases such as unconventional superconductivity, parity-violating magnet, quantum liquid crystal, and topological states of matter. In particular, our recent interest focuses on quantum phases lacking global or local space inversion symmetry. This year, we studied exotic superconductivity such as odd-parity superconductivity, odd-frequency superconductivity, noncentrosymmetric superconductivity, and ferroelectric superconductivity. Target materials include transition metal dichalcogenides such as MoS_2, heavy fermion superconductors such as UTe_2 and $CeRh_2As_2$, and perovskite oxides such as $SrTiO_3$. Interestingly, most of them are candidates of topological superconductors. We also explored new functionalities of superconductors and magnets. For instance, superconducting diode effect, giant surface Edelstein effect in d-wave superconductors, chiral photocurrent generation in parity-violating antiferromagnet, and nonlinear electric transport have been theoretically clarified, and candidate materials have been proposed.

Visiting Associate Professor

HIGASHI, Masahiro *(from Kyoto University)*

Theoretical Study on the Excited-State Reactions in Condensed Phases

We are theoretically investigating chemical reactions and physical properties in condensed phases such as solutions and proteins. In particular, we are focusing on the excited-state reactions in condensed phases. The excited-state reaction dynamics of large systems are still one of most challenging subjects in theoretical chemistry due to the high computational cost of quantum chemical calculations for excited states and adequate statistical samplings required for molecular dynamics simulations. To overcome these difficulties, we have been developing several efficient methods combining quantum chemical calculations and molecular dynamics simulations. Recently, we analyzed the excitation energy transfer in a light-harvesting complex by using our developed methods and found that the efficient excitation energy transfer is achieved by the site-dependent fluctuations. We are now investigating the primary charge separation in photosynthetic reaction centers and the photoexcited charge separation in organic solar cells. We will reveal molecular mechanisms of environmental effects in both systems.