



RESEARCH ACTIVITIES

Theoretical and Computational Molecular Science

It is our goal to develop new theoretical and computational methods based on quantum mechanics and statistical mechanics to predict and understand the structures, chemical reactions, and functions of molecules in gas and condensed phases including nano- and bio-systems.

Theoretical Studies on Heterogeneous Condensed Phase Dynamics

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Professional Employment

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Keywords Spatio-Temporal Heterogeneous Dynamics, Liquids, Proteins

Nonlinear intermolecular interactions cause complicated motions in condensed phases, *e.g.* liquids and biological systems. These motions are spatially and temporally heterogeneous with a wide range of time and spatial scales and yield both static and dynamic properties of the systems. In particular, heterogeneity plays important role in strongly-interacting systems, *e.g.* supercooled and ionic liquids, and biological systems. The spatio-temporal non-uniform motions known as dynamic heterogeneity are considered to be a clue to understand supercooled liquids and glass transition. Furthermore, heterogeneous reaction rates have been found in biological systems. Therefore, understanding of spatio-temporal heterogeneous dynamics is essential to the elucidation of the structure, thermodynamics, dynamics, and functions of the systems.

We have been investigating inter- and intra-molecular dynamics of water by third-order nonlinear spectroscopy which provide the detailed dynamics that are not available from conventional IR spectroscopy. We examined two-dimensional IR spectra and the energy relaxation and revealed the molecular mechanism of the ultrafast energy relaxation, which is one of dynamical features of water, *i.e.* the fast energy relaxation is caused by the nonlinear strong coupling between the libration motion and other intra- and inter-molecular vibrational motions.

We have also investigated the dynamics of supercooled liquids. We quantified the lifetime of dynamic heterogeneity by introducing the three-time correlation function of density

fluctuation, which is sensitive to the time evolution of dynamic heterogeneity. Our systematic analysis for various systems shows that the lifetime of dynamic heterogeneity is intimately related to configurational entropy and thus the temperature dependence of lifetime of dynamic heterogeneity is more sensitive to the fragility than that of α -relaxation time determined by one-time correlation function. In addition to the analysis of dynamic heterogeneity with multi-time correlation function, we have examined the molecular origin of anomalous temperature dependence of isobaric specific heat of water. The time scale involved in isothermal specific heat has been analyzed by analyzing complex specific heat. We examined the emergence of correlated motion in terms of the wave-number (k) dependent complex specific heat and the shell-wise energy fluctuation.

Currently, we are investigating how slow motions, which are involved in functions, are induced in biological molecules.

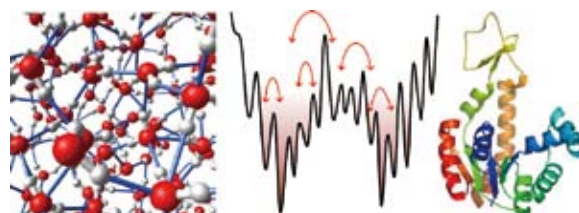


Figure 1. Schematic figure of rugged energy landscape (center) in supercooled water (left) and a biomolecule (right).

Selected Publications

- T. Yagasaki and S. Saito, *Acc. Chem. Res.* **42**, 1250–1258 (2009), *Annu. Rev. Phys. Chem.* **64**, 55–75 (2013).
- S. Imoto, S. Xantheas and S. Saito, *J. Chem. Phys.* **139**, 044503 (7 pages) (2013).
- K. Kim and S. Saito, *J. Chem. Phys. (Special Topic on Glass Transition)* **138**, 12A506 (12 pages) (2013).
- S. Saito, I. Ohmine and B. Bagchi, *J. Chem. Phys.* **138**, 094503 (7 pages) (2013).

1. Anomalous Dynamics of Supercooled Water in “No Man’s Land”

There exists no experimental study on dynamics of supercooled water between 155 K and 232 K, though several conjectures have been put forward. We carry out extensive molecular dynamics simulations from room temperatures down to as low as 130 K. Relaxation times are found to vary over twelve orders of magnitude in traversing this range, with occurrence of multiple anomalies. Structural, dynamical and thermodynamic properties all show a crossover, around 225 K, to a different, low density liquid state with different dynamical properties. On further cooling, this low density liquid again undergoes a dynamical transition around 197 K region where the density reaches its minimum, the dynamical heterogeneity starts to decrease after reaching maximum, and Stokes-Einstein relation, which is violated above 197 K, is recovered below 197 K. The temperature dependence of the relaxation times reveals three distinct branches, with discontinuities around 225 K and 197 K. From analysis of clusters of liquid-like and ice-like molecules, we attribute the latter anomalies to a pseudo-spinodal decomposition where the clusters of liquid-like molecules become fragmented (as if in a reverse percolation transition) and the small high density liquid droplets get surrounded by the dominant low density liquid. The third low temperature branch that appears below 197 K is studied here for the first time and is quite distinct from previous two branches. The relaxation time of this low temperature branch grows rapidly and the fitted relaxation time is projected to cross the 100 s mark around 135 K. We find that the number of defects in the liquid-like clusters serves as a good order parameter to describe this rapid growth. The approach to the amorphous ice is driven both by the rapid disappearance of the liquid-like droplets (below 180 K) and a simultaneous slow down of relaxation.

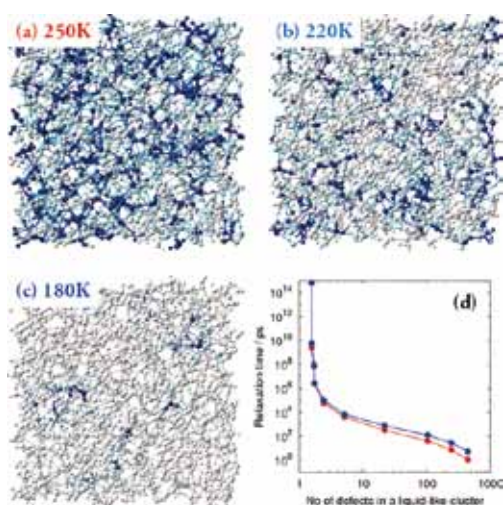


Figure 2. Snapshots of supercooled liquid water at (a) 250, (b) 220, and (c) 180 K. (d) Relationship between the number of molecules in a liquid-like cluster and the relaxation times of translational (red curve) and rotational (blue curve) motions. A liquid-like cluster consists of HB defects and their first hydration molecules. Colored molecules in (a)–(c) are liquid-like clusters.

2. Theoretical Study on Excited States of Bacteriochlorophyll *a* in Solutions with Density Functional Assessment

We investigate the excited-state properties of bacteriochlorophyll *a* (BChl *a*) in triethylamine, 1-propanol, and methanol by using the quantum mechanical and molecular mechanical (QM/MM) reweighting free energy SCF method, which is an efficient geometry optimization method of a QM subsystem on a QM/MM free energy surface. We employ the time-dependent density functional theory for the excited-state electronic structure calculations with several density functionals. However, no prevalent functional can reproduce the experimental results, *i.e.* the absorption and reorganization energies of BChl *a* in solutions. We optimize the parameter μ in the range-separated hybrid functionals to reproduce the differences of the absorption energies in three solvents. The CAM-B3LYP functional with $\mu = 0.20$ can also reproduce the reorganization energies in triethylamine almost quantitatively. We examine the origin of the difference of the absorption energies in the three solutions. It is considered that the density functional with an adjusted parameter is essential to the understanding of the excited-state properties of BChl *a* in proteins and also the mechanism of the photosynthetic systems.

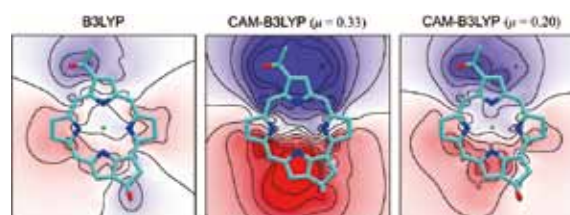


Figure 3. Functional dependence of the change in electrostatic potential of BChl *a* on the Q_y excitation in 1-propanol. The electrostatic potential distribution is calculated at the ground-state optimized geometry. Positive and negative values are shown by red and blue colors, respectively.

References

- 1) S. Saito, I. Ohmine and B. Bagchi, to be published.
- 2) M. Higashi, T. Kosugi, S. Hayashi and S. Saito, *J. Phys. Chem. B* (2014), in press.

Theory for Optical Near-Field Response and its Application to Functional Nanodevices

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Keywords Optical Near-Field, Light-Matter Interaction, Nanodevices

Optical response of molecules is undoubtedly essential for understanding their physicochemical properties. In conventional theoretical approaches to optical response of molecules, two conditions are usually assumed: (i) Wavelength of incident light is considered to be much longer than molecular size, *i.e.*, dipole approximation. Thus, a target molecule is well approximated by a point dipole and the dipole feels a uniform electromagnetic field. (ii) Electric polarization in a molecule induced by incident-light excitation inevitably generates a new electromagnetic field, referred to as an “optical near-field,” according to Maxwell’s equations. However, such a self-consistent light-matter (LM) interaction between electron and electromagnetic field dynamics is ignored. Recent development of nanofabrication and nano-optical techniques requires a more general optical response theory fully taking account of *nonuniform and self-consistent* light-matter (LM) interactions.

We have developed a generalized theoretical description of full (nonuniform and self-consistent) LM interactions with the aim of understanding the optical near-field excitation dynam-

ics in nanostructures of more than ten-nanometers in size. Electron dynamics in nanostructures interacting with an electromagnetic field is described by the time-dependent Kohn-Sham (TDKS) equation based on minimal coupling Hamiltonian with Coulomb gauge. On the other hand, electromagnetic field dynamics is represented by the microscopic Maxwell’s equations. The nonuniform LM interaction is taken into account in the vector potential and the self-consistent LM interaction is described by solving the electron and electromagnetic field coupled equations self-consistently. The coupled equations are solved numerically by using our developed computational program (GCEED: *Grid-based Coupled Electron and Electromagnetic field Dynamics*). Our computational approach is based on a finite-difference method in real-time and real-space. Since the approach employs very simple algorithms, it is very suitable for massively parallelized computations. We have achieved the parallelized calculations with more than 660,000 cores in the K computer (Kobe RIKEN), which is one of the worldwide leading supercomputers.

Selected Publications

- K. Nobusada and K. Yabana, “Photoinduced Electric Currents in Ring-Shaped Molecules by Circularly Polarized Laser Pulses,” *Phys. Rev. A* **75**, 032518 (7 pages) (2007).
- T. Iwasa and K. Nobusada, “Nonuniform Light-Matter Interaction Theory for Near-Field-Induced Electron Dynamics,” *Phys. Rev. A* **80**, 043409 (11 pages) (2009).
- Y. Kubota and K. Nobusada, “Exciton–Polariton Transmission in Quantum Dot Waveguides and a New Transmission Path due to Thermal Relaxation,” *J. Chem. Phys.* **134**, 044108 (8 pages) (2011).

1. Massively-Parallel Electron Dynamics Calculations in Real-Time and Real-Space: Toward Applications to Nanostructures of More Than Ten-Nanometers in Size¹⁾

A highly efficient program of massively parallel calculations for electron dynamics has been developed in an effort to apply the method to optical response of nanostructures of more than ten-nanometers in size. The approach is based on time-dependent density functional theory calculations in real-time and real-space. The computational code is implemented by using simple algorithms with a finite-difference method in space derivative and Taylor expansion in time-propagation. Since the computational program is free from the algorithms of eigenvalue problems and fast-Fourier-transformation, which are usually implemented in conventional quantum chemistry or band structure calculations, it is highly suitable for massively parallel calculations. Benchmark calculations using the K computer at RIKEN demonstrate that the parallel efficiency of the program is very high on more than 60,000 CPU cores. The method is applied to optical response of arrays of C₆₀ orderly nanostructures of more than 10 nm in size. The computed absorption spectrum is in good agreement with the experimental observation.

The present computation is one of the largest first-principles calculations of photoinduced electron dynamics in nanostructures. It is highly expected that nanostructures of up to ~50 nm in size with a quantum confinement effect are promising materials in developing next-generation quantum devices with valuable functions. The first-principles calculations of excitation dynamics in such huge nanostructures are really unprecedented in molecular and material science. The present computational approach paves a new way of theoretically designing these devices at a real nanoscale.

2. First-Principles Computational Visualization of Localized Surface Plasmon Resonance in Gold Nanoclusters²⁾

We have studied the cluster-size dependence of localized surface plasmon resonance (LSPR) for Au_n clusters of up to $n = 1414$ (3.9 nm in diameter) by performing first-principles photoinduced electron dynamics calculations. The maximum cluster size is unprecedentedly large in comparison with those addressed in previous, fully quantum mechanical, calculations of optical response in real cluster systems. The computations enable us to see that LSPR gradually grows and its peak position redshifts (blueshifts) with increasing (decreasing) cluster size. These computed results are in good agreement with experimental observations. The localized surface charge distributions are visualized in real space, vividly illustrating the conduction electrons oscillate in a collective manner. From the visualization, LSPR has proven to be discernible at $n \sim 146$, although the optical responses for Au_n ($n \leq 146$) are still

mostly in a quantum regime because a quantum confinement effect remains predominant. The charge oscillation occurs in two regions, the outermost surface region and the inner region. The surface charge responds in synchronization with the applied laser field, whereas the inner charge oscillates locally around each gold atom in a direction opposite to the surface charge distribution. This is clear evidence of a screening effect caused by the d-electrons. The present quantum mechanically accurate description of LSPR in gold nanoclusters provides valuable information when utilizing the properties of LSPR in developing plasmonic functional devices.

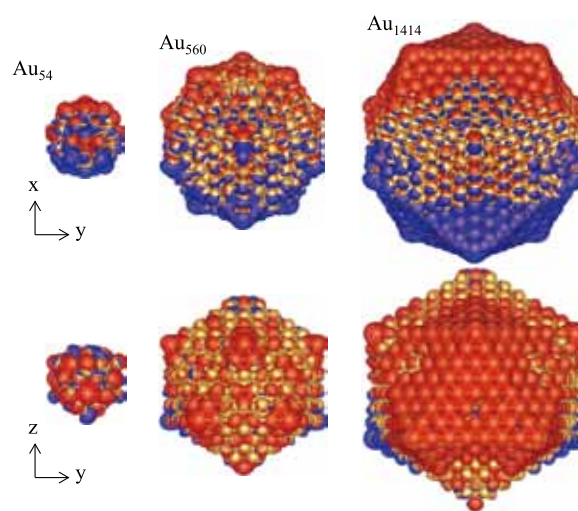


Figure 1. Photoinduced densities of LSPR for Au_n ($n = 54, 560, \text{ and } 1414$).

3. Nonsuperatomic [Au₂₃(SC₆H₁₁)₁₆]⁻ Nanocluster Featuring Bipyramidal Au₁₅ Kernel and Trimeric Au₃(SR)₄ Motif³⁾

We report the X-ray structure of a cyclohexanethiolate-capped [Au₂₃(SR)₁₆]⁻ nanocluster (counterion: tetraoctylammonium, TOA⁺). The structure comprises a cuboctahedron-based bipyramidal Au₁₅ kernel, which is protected by two staple-like trimeric Au₃(SR)₄ motifs, two monomeric Au(SR)₂ and four plain bridging SR ligands. Electronic structure analysis reveals nonsuperatomic feature of [Au₂₃(SR)₁₆]⁻ and confirms the Au₁₅ kernel and surface motifs. The Au₁₅ kernel and trimeric staple motif are unprecedented and offer new insight in understanding the structure evolution of gold nanoclusters.

References

- 1) M. Noda, K. Ishimura, K. Nobusada, K. Yabana and T. Boku, *J. Comput. Phys.* **265**, 145–155 (2014).
- 2) K. Iida, M. Noda, K. Ishimura and K. Nobusada, *J. Phys. Chem. A* **118**, 11317–11322 (2014).
- 3) A. Das, T. Li, K. Nobusada, C. Zeng, N. L. Rosi and R. Jin, *J. Am. Chem. Soc.* **135**, 18264–18267 (2013).

Advanced Electronic Structure Theory in Quantum Chemistry

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Education

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Awards

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2009 The Wiley-International Journal of Quantum Chemistry Young Investigator Award
2013 Laureate, International Academy of Quantum Molecular Science
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Keywords

Electronic Structure Theory, Quantum Chemistry, Computational Chemistry

Computational quantum chemistry, that is, practicing quantum chemical theory using computers, is now considered to be a powerful means to provide detailed analysis of chemical phenomena. The focus of our group is to develop methods and algorithms of molecular electronic structure calculations, which are capable of supplying electronic-level interpretation and reliable prediction of chemical characters, reactivity, energetics, and spectroscopic properties of molecular systems. Also, we are interested in applying the methods to challenging chemical systems. Recently, we have developed advanced multireference methods to describe highly-correlated many-electron wavefunction, which cannot be qualitatively accounted for with mean-field or one-electron theory (*e.g.*, density functional theory). The multireference wavefunction need be represented with a quantum superposition of multiple electron configurations; however, this gives rise to a high computational expense because the degree of the superposition is in general exponentially dependent on the system size. We approach the multireference problems using the density matrix renormalization group (DMRG), which is originally a method of condensed matter physics to solve strong correlation phenomena in physical models. We developed an efficient implementation for adapting DMRG to quantum chemical calcula-

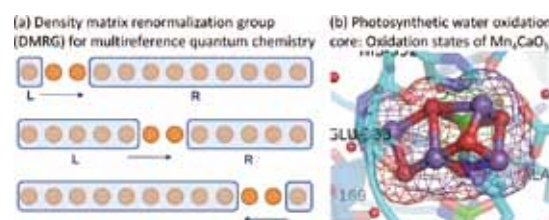


Figure 1. (a) Algorithm of density matrix renormalization group (DMRG) and (b) Its application to manganese cluster.

tion, in which the DMRG is exploited to describe static correlation in combination with the complete active space (CAS) model. Our DMRG-based methods have shown to be capable of handling very large correlation space, which far exceeds the limitation of conventional methods. We have further introduced a scheme to additively account for dynamic correlation on top of active-space DMRG wavefunction. Using these methods, we carried out chemical applications to multireference electronic systems, ranging from organic material molecules, such as radicals of graphene nanoribbons, to transition metal complexes, such as tetranuclear manganese cluster.

Selected Publications

- Y. Kurashige and T. Yanai, "High-Performance *Ab Initio* Density Matrix Renormalization Group Method: Applicability to Large-Scale Multireference Problems for Metal Compounds," *J. Chem. Phys.* **130**, 234114 (21 pages) (2009).
- W. Mizukami, Y. Kurashige and T. Yanai, "More π Electrons Make a Difference: Emergence of Many Radicals on Graphene Nanoribbons Studied by *Ab Initio* DMRG Theory," *J. Chem. Theory Comput.* **9**, 401–407 (2013).
- Y. Kurashige, G. K-L. Chan and T. Yanai, "Entangled Quantum Electronic Wavefunctions of the Mn_4CaO_5 Cluster in Photosystem II," *Nat. Chem.* **5**, 660–666 (2013).

1. Radical O–O Coupling Reaction in Diferrate-Mediated Water Oxidation Studied with Multireference Wave Function Theory¹⁾

Recently, the water oxidation catalyzed by potassium ferrate K_2FeO_4 was investigated on the basis of experimental kinetic isotope effect analysis assisted by density functional calculations, revealing the intramolecular oxo-coupling mechanism within a di-iron(VI) intermediate, or diferrate [Sarma *et al.*, *J. Am. Chem. Soc.* **134**, 15371 (2012)]. Here, we reported a detailed examination of this diferrate-mediated O–O bond formation using scalable multireference electronic structure theory. High-dimensional correlated many-electron wave functions beyond one-electron picture were computed with *ab initio* DMRG method along the O–O bond formation pathway. The necessity of using large active space arises from the description of complex electronic interactions and varying redox states both associated with two-center antiferromagnetic multivalent iron–oxo coupling. Dynamic correlation effects on top of the active space DMRG wave functions were additively accounted for by complete active space second-order perturbation (CASPT2) and multireference configuration interaction (MRCI) based methods, which were recently introduced by our group. These multireference methods were capable of handling the double shell effects in the extended active space treatment. The calculations with CAS(36e,32o), which is far over conventional limitation, provide a quantitatively reliable prediction of potential energy profiles and confirmed the viability of direct oxo coupling. (Figure 2).

2. Toward Reliable Prediction of Hyperfine Coupling Constants Using *Ab Initio* Density Matrix Renormalization Group Method²⁾

The DMRG method was used in conjunction with the CASCI and CASSCF methods to evaluate hyperfine coupling constants (HFCCs) for a series of diatomic $^2\Sigma$ radicals (BO, CO⁺, CN, and AlO) and vinyl (C₂H₃) radical. The electron correlation effects on the computed HFCC values were systematically investigated using various levels of active space, which were increasingly extended from single valence space to large-size model space entailing double valence and at least single polarization shells. In addition, the core correlation was treated by including the core orbitals in active space. Reasonably accurate results were obtained by the DMRG-CASSCF method involving orbital optimization, while DMRG-CASCI calculations with Hartree-Fock orbitals provided poor agreement of the HFCCs with the experimental values. To achieve further insights into the accuracy of HFCC calculations, the orbital contributions to the total spin density were analyzed at a given nucleus, which is directly related to the FC term and is numerically sensitive to the level of correlation treatment and basis sets. This work serves as the first study on the perfor-

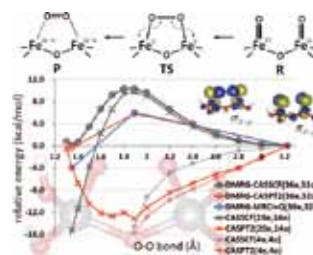


Figure 2. Diferrate-mediated O–O bond formation was studied using *ab initio* DMRG theory with large-size active space CAS(36e,32o) in conjunction with dynamic correlation correction.

mance of the *ab initio* DMRG method for HFCC prediction.

3. Flexible Nuclear Screening Approximation to the Two-Electron Spin–Orbit Coupling Based on *Ab Initio* Parameterization³⁾

The derivation, implementation, and validation of a new approximation to the two-electron spin–orbit coupling (SOC) terms was reported. The approximation, referred to as flexible nuclear screening spin–orbit (FNSSO), is based on the effective one-electron spin–orbit operator and accounts for two-electron SOC effects by screening nuclear charges. A highly flexible scheme for the nuclear screening is developed, mainly using parameterization based on *ab initio* atomic SOC calculations. Tabulated screening parameters are provided for contracted and primitive Gaussian-type basis functions of the ANO-RCC basis set for elements from H to Cm. A model to correct for the effect of spin–orbit splitting of transition metal *d* orbitals on their SOC matrix elements was introduced. The method is applied to a representative set of molecules, and compared to exact treatment and other approaches at the same level of relativistic theory. The calculated SOC matrix elements are in very good agreement with their “exact” values; deviation below 1% is observed on average.

References

- 1) Y. Kurashige, M. Saitow, J. Chalupský and T. Yanai, *Phys. Chem. Chem. Phys.* **16**, 11988–11999 (2014).
- 2) L. N. Tran, Y. Kurashige and T. Yanai, *J. Chem. Theory Comput.* **10**, 1953–1967 (2014).
- 3) J. Chalupský and T. Yanai, *J. Chem. Phys.* **139**, 204106 (14 pages) (2013).
- 4) F. Liu, Y. Kurashige, T. Yanai and K. Morokuma, *J. Chem. Theory Comput.* **9**, 4462–4469 (2013).
- 5) Y. Kurashige, *Mol. Phys.* **112**, 1485–1494 (2014).
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- 7) T. V. Harris, Y. Kurashige, T. Yanai and K. Morokuma, *J. Chem. Phys.* **140**, 054303 (10 pages) (2014).

Awards

YANAI, Takeshi; Laureate, International Academy of Quantum Molecular Science 2013.
 YANAI, Takeshi; Young Scientist Awards of the Japan Society for Molecular Science 2013.
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Theoretical Study on Photochemistry and Catalysis

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Education

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Keywords

Quantum Chemistry, Photophysical Chemistry, 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 nanocluster catalysis

Metal nanoclusters supported by metal oxides or polymers achieves 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 hetero-junction of Ag nanocluster supported by alumina surface in terms of H₂ 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 H₂ Activation at Ag Cluster/θ-Al₂O₃ Dual Perimeter Sites: A DFT Study," *J. Phys. Chem. C* **118**, 7996–8006 (2014).

1. Perturbative PCM SAC-CI Method

Ultraviolet-visible spectroscopies of molecules are commonly measured in solutions. Polar solvents are often used for solubility; solvent effects on the spectra are, therefore, considerable. Quantum chemical methods are useful for assigning and understanding the spectra and excited-state properties. For efficient calculations of the electronic excitations and absorption spectra of molecules in solutions, a perturbative approximation of the state specific polarizable continuum model (PCM) symmetry-adapted cluster configuration interaction (SAC-CI) method is proposed. This first-order PCM SAC-CI method considers the solvent effects on the energies of excited states up to the first-order with using the zeroth-order wavefunctions. This method can avoid the costly iterative procedure of the self-consistent reaction field (SCRF) calculations. The first-order PCM SAC-CI calculations well reproduce the results obtained by the iterative method for various types of excitations of molecules in polar and nonpolar solvents. The first-order contribution is significant for the excitation energies. The results obtained by the zeroth-order PCM SAC-CI, which considers the fixed ground-state reaction field for the excited-state calculations, are deviated from the results by the iterative method about 0.1 eV, and the zeroth-order PCM SAC-CI cannot predict even the direction of solvent shifts in *n*-hexane for many cases.

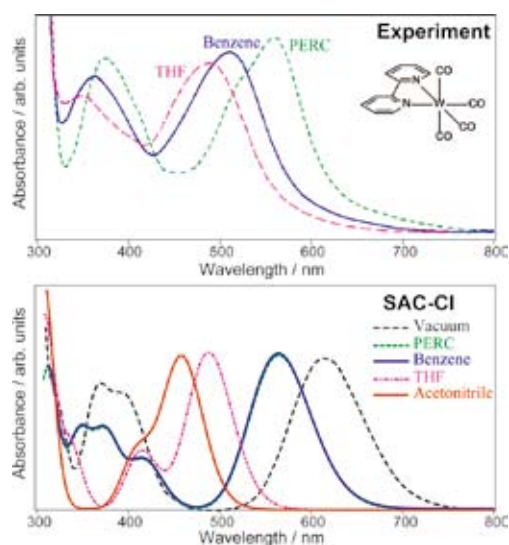


Figure 1. The observed and SAC-CI simulated absorption spectra of $W(CO)_4(bpy)$.

The first-order PCM SAC-CI is applied to studying the solvatochromisms of (2,2'-bipyridine)tetracarbonyltungsten [$W(CO)_4(bpy)$, bpy = 2,2'-bipyridine] and bis(pentacarbonyl tungsten)pyrazine [$(OC)_5W(pyrazine)W(CO)_5$, pyz = pyrazine]. The SAC-CI calculations reveal the detailed character of the excited states and the mechanisms of solvent shifts. The energies of metal to ligand charge transfer (MLCT) states are

significantly sensitive to solvents. The first-order PCM SAC-CI well reproduces the observed absorption spectra of the tungsten carbonyl complexes in several solvents.

2. H₂ Activation on Ag/Al₂O₃ Dual Perimeter Sites

The catalytic activity of supported metal nanoparticles depends on the metal-support interaction and metal size. Supported silver nanoparticles have been the focus of research because of their characteristic catalytic activity. This work aims to theoretically elucidate the role of the interface perimeter site between the Ag cluster and alumina support for H₂ dissociation by applying the periodic density functional theory (DFT) calculations.

H₂ dissociation by Ag clusters supported on the θ -Al₂O₃ (110) surface has been investigated using DFT calculations. The crucial role of the dual perimeter site of Ag cluster and the surface oxygen (O) site of the alumina support is demonstrated with three theoretical models: anchored cluster, isolated cluster, and anchored cluster on hydroxylated alumina. The heterolytic cleavage of H₂ at the silver–alumina interface, yielding Ag[−]H^{δ−} and O[−]H^{δ+}, is thermodynamically and kinetically preferred compared with H₂ cleavage at two Ag atomic sites on top of the Al₂O₃-supported Ag cluster and the homolytic cleavage of H₂ on the isolated Ag cluster. The hydroxylation at the O site of the alumina reduces the H₂ dissociation activity, which indicates that the interfacial bare O site is indispensable. It is concluded that the interfacial cooperative mechanism between the Ag cluster and Lewis acid-base pair site (bare Al–O site) is essentially relevant for the H₂ activation over Ag-loaded Al₂O₃ catalysts.

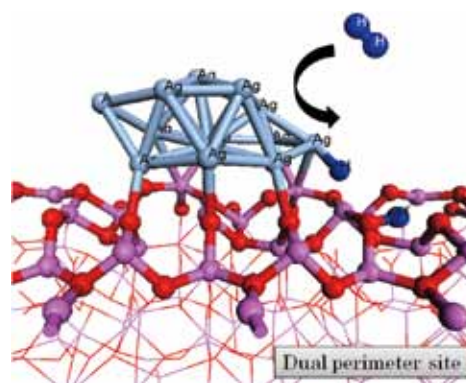


Figure 2. Ag₁₃ cluster on θ -Al₂O₃(110) surface. A model for investigating H₂ activation mechanisms with DFT calculations.

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Development of New Molecular Dynamics Algorithms for Biomolecular Systems

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2002 Postdoctoral Fellow, The University of Tokyo
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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.

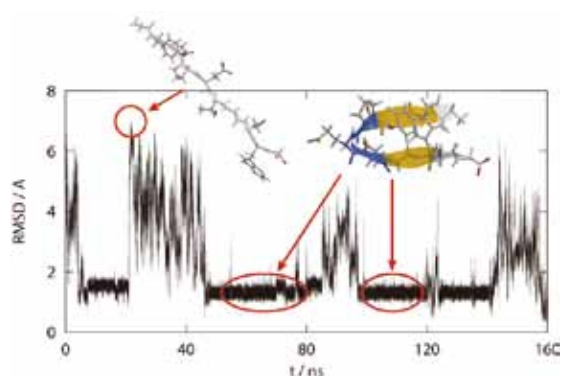


Figure 1. Time series of protein folding simulation.

We are also interested in amyloid fibrils, which are insoluble aggregates of misfolded fibrous proteins and associated with more than 20 human neurodegenerative diseases (Figure 2). For example, Alzheimer's disease is related to amyloid- β ($A\beta$) peptides. To overcome these diseases, it is essential to understand amyloid genesis and disruption. We perform such MD simulations of amyloid fibrils.

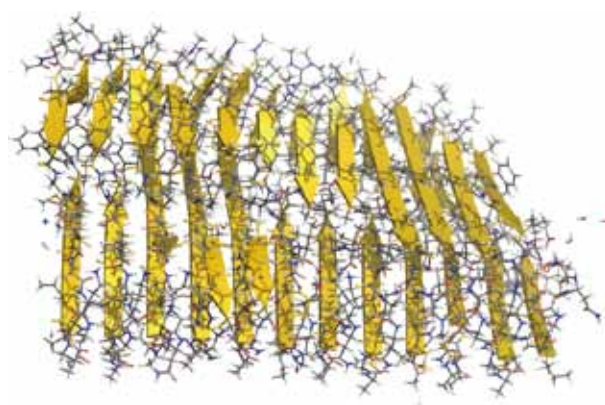


Figure 2. Snapshot of amyloid fibril.

Selected Publications

- H. Okumura and S. G. Itoh, "Amyloid Fibril Disruption by Ultrasonic Cavitation: Nonequilibrium Molecular Dynamics Simulations," *J. Am. Chem. Soc.* **136**, 10549–10552 (2014).
- 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).
- Y. Mori and H. Okumura, "Pressure-Induced Helical Structure of a Peptide Studied by Simulated Tempering Molecular Dynamics Simulations," *J. Phys. Chem. Lett.* **4**, 2079–2083 (2013).
- H. Okumura, "Temperature and Pressure Denaturation of Chignolin: Folding and Unfolding Simulation by Multibaric-Multi-thermal Molecular Dynamics Method," *Proteins* **80**, 2397–2416 (2012).

1. Amyloid Fibril Disruption by Ultrasonic Cavitation: Nonequilibrium Molecular Dynamics Simulations

There are some experimental reports that cavitation disrupts amyloid fibrils. However, it is still unknown how the cavitation or bubble in water disrupts the amyloid fibrils at atomic level. In order to answer this problem, we performed nonequilibrium molecular dynamics simulations of an A β fibril in explicit water.¹⁾ We used twelve A β (17–42) peptide molecules, 10169 water molecules, and twelve sodium ions as counter ions. The simulation was started from the experimentally-known amyloid oligomer structure in the amyloid fibril. To express supersonic wave, sinusoidal pressure was applied between –100 MPa and 300 MPa. Snapshots of this simulation are illustrated in Figure 3. When the pressure was decreased to a negative value of –100 MPa from a room pressure, a bubble formation was observed around the transmembrane region, in which all the amino acid residues were hydrophobic. Even after the bubble size increased, the secondary structures of the oligomer were maintained. When the pressure was increased to a positive value, the bubble shrank and collapsed, and the oligomer was disrupted. At this time, most water molecules attacked the hydrophilic residues in nontransmembrane region.

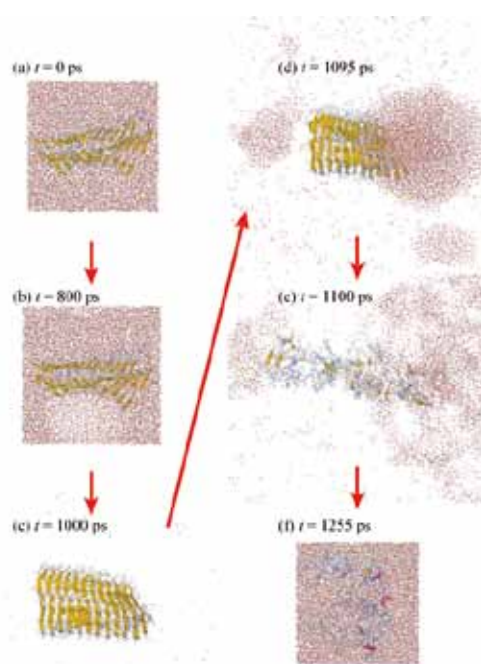


Figure 3. Snapshots of the non-equilibrium MD simulation of the amyloid- β fibril in explicit water.

2. Development of Hamiltonian Replica-Permutation Method

We propose the Hamiltonian replica-permutation method (RPM) (or multidimensional RPM) for molecular dynamics and Monte Carlo simulations, in which parameters in the Hamiltonian are permuted among more than two replicas with the Suwa-Todo algorithm.²⁾ We apply the Coulomb RPM, which is one of realization of the Hamiltonian RPM, to an alanine dipeptide and to two amyloid- β (29–42) molecules. The Hamiltonian RPM realizes more efficient sampling than the Hamiltonian replica-exchange method. We illustrate the protein misfolding funnel of amyloid- β (29–42) and reveal its dimerization pathways.

3. Manifold Correction Method for the Nosé-Hoover and Nosé-Poincaré Molecular Dynamics Simulations

We introduce the manifold correction method to MD simulations with the Nosé-Hoover and Nosé-Poincaré thermostats.³⁾ The manifold correction method was originally developed in astronomy, as an accurate numerical method for many body systems. Because the Nosé-Hoover thermostat is not a symplectic algorithm, the quantity which is conserved analytically is not conserved but increases in actual MD simulations. Using the manifold correction method, this quantity is completely conserved, and it makes the MD simulation stable. Because the conservation of this quantity is required in the proof that the Nosé-Hoover thermostat gives the canonical ensemble, the manifold correction method guarantees to provide the correct statistical ensemble. Although the time development of the Nosé-Poincaré thermostat is described as a symplectic algorithm, if the interatomic potential energy is truncated, the Nosé-Poincaré thermostat is no longer symplectic. In this case, the Hamiltonian increases, and temperature cannot be controlled. Applying the manifold correction method to the Nosé-Poincaré thermostat, the Hamiltonian becomes conserved and temperature can be appropriately controlled.

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Theory and Computation of Reactions and Properties in Solutions and Liquids

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We currently focus on the projects both on ultrafast photoinduced electron energy transfer in the excited state in solution and on ionic liquids (ILs). The project on photoinduced electron energy transfer processes in the excited state in solution is aimed at the development of a theoretical method to describe electron energy transfer including solvent motion and dynamics. On the other hand, ILs' projects concentrate the study of dynamical properties on ionic liquids using molecular dynamics simulation technique.

1. The Theoretical Investigation of Photoinduced Electron Energy Transfer Processes in the Excited State in Solution

We have developed a procedure for tracing the time-dependent evolution of the electronic structure of a solute molecule in solution, coupling an electronic structure theory with solvent motion. We have extended this method for investigating electron energy transfer processes in the excited state

in solution. It is shown that the coupling between solvation dynamics and a fast intramolecular electron energy transfer is likely to play an important role in the emergence of photo-induced unique functionalities in biochemical and metal complex systems.

2. Investigations of Dynamical Properties on Ionic Liquids¹⁻²⁾

We focus on, in particular, the dynamical properties on ionic liquids (ILs). With molecular dynamics simulation, it has been found out that ILs indicate unique collective dynamics. We have investigated interesting dynamical heterogeneity in ILs at room temperature. Also, we have studied spatial heterogeneity.

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Visiting Professors



Visiting Professor
TEN-NO, Seiichiro (from *Kobe University*)

New Frontier of Hybrid Stochastic and Deterministic Electronic Structure Approaches

The vast majority of ab initio electronic structure methods are on the basis of deterministic disciplines, in which a compactification of an N-factorial CI expansion is of main interest. Nevertheless, the way to calculate strongly correlated systems with quasi-degeneracy and general excited states accurately still remains open. These objectives are of significant importance for entangled electronic states involving photoinduced phenomena in biochemistry and energy conversion processes in chemistry. We have recently developed the model space quantum Monte Carlo (MSQMC) method crossing the effective Hamiltonian formalism and full configuration interaction (FCI) QMC [*ST, J. Chem. Phys.* **138**, 164126 (2013)]. The method sidesteps the negative sign problem in QMC arising from quasi-degeneracy transcending the storage limitation for CI vectors. Promising results are obtained for the FCI potential energy curves of various excited states for C₂, N₂, and O₂ molecules [Y. Ohtsuka and *ST*, unpublished (2014)]. The method has been also applied to the oxygen evolving center of the photo system II for low-lying spin states.



Visiting Professor
TAKADA, Shoji (from *Kyoto University*)

Computational Studies of Biomolecular Systems

I am studying in the area of computational molecular biophysics, primarily focusing on protein structure and dynamics. Even though thousands of X-ray crystal structures may provide impression that biomolecules are rigid material, in reality they are nano-scale molecules that work under thermal noise and, as such, they are dynamic. Given many crystal structures as snapshots, my ultimate goal is to understand dynamical functions of these molecules via computational analysis. Specifically, my current research includes 1) protein folding and conformational dynamics, 2) biomolecular motors, and 3) gene dynamics, together with 4) methodology development used in these topics. Protein folding and conformational dynamics is a basis to understand all the protein functions. Many proteins undergo substantial conformational change upon binding to their partner molecules, which form a molecular switch. How these molecular switch is regulated is, in my view, one of the most fundamental problems in protein science.



Visiting Associate Professor
SUGIMOTO, Manabu (from *Kumamoto University*)

Computational Molecular Science for Chemical Design and Engineering

The quantum chemical method is a powerful and insightful tool for analyzing and predicting molecular structures and chemical phenomena. Our group is interested in applying electronic-structure methods for investigating molecular functions that are of practical importance. Our on-going research is twofold: One is direct application of the quantum methods. Recently we have been studying spectral properties of supramolecular metal-ion sensors in collaboration with experimentalists. We have been successful to reveal the electronic mechanism for metal-ion sensing. We are also studying photochemical water splitting by graphitic carbon nitride. Its chemical property is expected to provide rich information for designing artificial photosynthesis. Another research is for development of chemoinformatics through which one would be able to learn, understand, investigate, predict, and design molecules and their chemistries. We are developing a system on the basis of our original electronic-structure database and new search engines. Our contribution is intended to enrich usefulness and uniqueness of Computational Molecular Science.