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 Correlated Dynamics in Condensed Phases

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Liquids and biological systems show complicated dynamics because of their structural flexibility and dynamical hierarchy. Understanding these complicated dynamics is indispensable to elucidate chemical reactions, thermodynamical and dynamical properties in solutions, and functions of proteins. We have been investigating ultrafast fluctuations and relaxation dynamics in liquid water and solution by using linear and nonlinear spectroscopy.[1–4] In addition, we have been studying heterogeneous dynamics in supercooled liquids in terms of multi-time correlation function[5] and the molecular origin of anomalous thermodynamic properties of supercooled water.[6]

1. Fluctuations and Relaxation Dynamics of Liquid Water Revealed by Linear and Nonlinear Spectroscopy[1]

Many efforts have been devoted to elucidating the intra- and intermolecular dynamics of liquid water because of their important roles in many fields of science and engineering. Nonlinear spectroscopy is a powerful tool to investigate the dynamics. Because nonlinear response functions are described by more than one time variable, it is possible to analyze static and dynamic mode couplings. Here we review the intra- and intermolecular dynamics of liquid water revealed by recent linear and nonlinear spectroscopic experiments and computer simulations. In particular, we discuss the population relaxation, anisotropy decay, and spectral diffusion of the intra- and intermolecular motions of water and their temperature dependence, which play important roles in ultrafast dynamics and relaxations in water.

2. Molecular Origin of the Difference in the HOH Bend of the IR Spectra between Liquid Water and Ice[2]

The intensity of the HOH bend in the infrared (IR) spectrum of ice is significantly smaller than the corresponding one in liquid water. This difference in the IR intensities of the HOH bend in the two systems is investigated using Molecular Dynamics (MD) simulations with the flexible, polarizable, *ab intio* based TTM3-F model for water, a potential that correctly reproduces the experimentally observed increase of the HOH angle in liquid water and ice from the water monomer value. We have identified two factors that are responsible for the difference in the intensity of the HOH bend in liquid water and ice: (i) the decrease of the intensity of the HOH bend in ice caused by the strong anti-correlation between the permanent dipole moment of a molecule and the induced dipole moment of neighboring hydrogen bond acceptor molecules, and (ii) the weakening of this anti-correlation by the disordered hydrogen bond network in liquid water. The presence of the anti-correlation in ice is further confirmed by *ab intio* electronic structure calculations of water pentamer clusters extracted from the trajectories of the MD simulations with the TTM3-F potential for ice and liquid water.

3. Ultrafast Dynamics of Liquid Water: Frequency Fluctuations of the OH Stretch and the HOH Bend[3)]

Frequency fluctuations of the OH stretch and the HOH bend in liquid water are reported from the third-order response function evaluated using the TTM3-F potential for water. The simulated two dimensional infrared spectra of the OH stretch are similar to previously reported theoretical results. The present study suggests that the frequency fluctuation of the HOH bend is faster than that of the OH stretch. The ultrafast loss of the frequency correlation of the HOH bend is due to the strong couplings with the OH stretch as well as the intermolecular hydrogen bond bend.

4. Multiple Length and Time Scales of Dynamic Heterogeneities in Model Glass-Forming Liquids: A Systematic Analysis of Multi-Point and Multi-Time Correlations[5)]

We report an extensive and systematic investigation of the multi-point and multi-time correlation functions to reveal the spatio-temporal structures of dynamic heterogeneities in glass-forming liquids. Molecular dynamics simulations are carried out for the supercooled states of various prototype models of glass-forming liquids such as binary Kob–Andersen, Wahnström, soft-sphere, and network-forming liquids. While the first three models act as fragile liquids exhibiting super-Arrhenius temperature dependence in their relaxation times, the last is a strong glass-former exhibiting Arrhenius behavior. First, we quantify the length scale of the dynamic heterogeneities utilizing the four-point correlation function. The growth of the dynamic length scale with decreasing temperature is characterized by various scaling relations that are analogous to the critical phenomena. We also examine how the growth of the length scale depends upon the model employed. Second, the four-point correlation function is extended to a three-time correlation function to characterize the temporal structures of the dynamic heterogeneities based on our previous studies [K. Kim and S. Saito, *Phys. Rev. E* **79**, 060501(R) (2009); *J. Chem. Phys.* **133**, 044511 (2010)]. We provide comprehensive numerical results obtained from the three-time correlation function for the above models. From these calculations, we examine the time scale of the dynamic heterogeneities and determine the associated lifetime in a consistent and systematic way. Our results indicate that the lifetime of the dynamical heterogeneities becomes much longer than the α-relaxation time determined from a two-point correlation function in fragile liquids. The decoupling between the two time scales is remarkable, particularly in supercooled states, and the time scales differ by more than an order of magnitude in a more fragile liquid. In contrast, the lifetime is shorter than the α-relaxation time in tetrahedral network-forming strong liquid, even at lower temperatures.

5. Frequency Dependence of Specific Heat in Supercooled Liquid Water and Emergence of Correlated Dynamics[6)]

Molecular origin of the well-known specific heat anomaly in supercooled liquid water is investigated here by using extensive computer simulations and theoretical analyses. A rather sharp increase in the values of isobaric specific heat with lowering temperature and the weak temperature dependence of isochoric specific heat in the same range are reproduced in simulations. We calculated the spatio-temporal correlation among temperature fluctuations and examined the frequency dependent specific heat. The latter shows a rapid growth in the low frequency regime as temperature is cooled below 270 K. In order to understand the microscopic basis of this increase, we have performed a shell wise decomposition of contributions of distant molecules to the temperature fluctuations in a central molecule. This decomposition reveals the emergence, at low temperatures, of temporally slow, spatially long ranged large temperature fluctuations. The temperature fluctuation time correlation function (TFCF) can be fitted to a William-Watts stretched exponential form with the stretching parameter close to 0.6 at low temperatures, indicating highly non-exponential relaxation. Temperature dependence of the relaxation time of the correlation function can be fitted to Vogel-Fulcher-Tamermann expression which provides a quantitative measure of the fragility of the liquid. Interestingly, we find that the rapid growth in the relaxation time of TFCF with lowering temperature undergoes a sharp crossover from a markedly fragile state to a weakly fragile state around 220 K.

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Photoinduced Electron Dynamics in Nanostructures

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We have developed theoretical methods to calculate photoinduced electron dynamics in nanoclusters. Furthermore, a highly efficient computational program of massively parallel calculations for electron dynamics has been developed to investigate optical response of nanostructures of more than ten-nanometers in size. More specifically, we have achieved electron dynamics simulations with the maximum size of 82,944 nodes (663,552 cores) on the K computer at RIKEN. We have also presented a theoretical method to investigate electrochemical processes on the basis of a finite temperature density functional theory (FT-DFT) approach combined with our recently developed open-boundary cluster model (OCM). In addition, structural and electronic properties of gold-thiolate clusters have been elucidated in collaboration with an experimental group.

1. Raman Enhancement by Plasmonic Excitation of Structurally-Characterized Metal Clusters: Au_8, Ag_8, and Cu_8

We have investigated the plasmonic excitations in small group-11element (Au, Ag, and Cu) clusters on the basis of ab initio electronic structure theory.[1)] Unlike alkali metal clusters,[2)] the plasmonic excitations mainly formed with (s,p) orbitals are affected by the inner d-electron excitations. The energy splitting between d and (s,p) levels is the largest for the silver atom among Au, Ag, and Cu, and thus the most intense plasmon in the BOCT M_8 cluster is formed for Ag_8. However, the structural modification to the linear isomer was found to give potential abilities as an optical sensitizer even for gold and copper clusters having nearly degenerate (d,s,p) energy levels. The linear cluster is highly anisotropic and gives multiple plasmonic modes along the molecular axis in the low excitation energy corresponding to the visible light. By utilizing the multiple excitations in the visible region, one can use this material as a universal optical sensitizer available for incident lights with various wavelengths.

As an example of sensitizing, we demonstrated the Raman enhancement of a pyrazine molecule by the linear and BOCT Au_8 clusters. The linear Au_8 cluster has a higher potential for both an enhancement intrinsic to the details of its electronic structures and an enhancement due to its robustness to altering the pyrazine–Au_8 intermolecular distance. It should be emphasized that recent development in experiments allows us to construct such an artificial linear structure on surfaces. We conclude that the structured nanoclusters are a promising strategy for designing effective optical sensitizers.

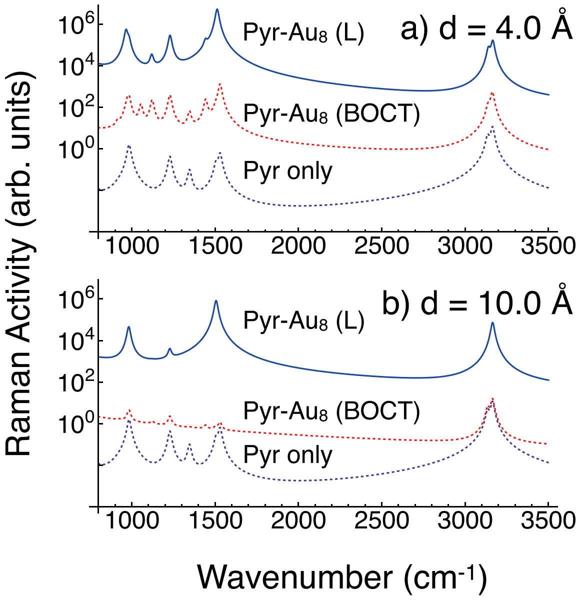

Figure 1. Raman vibrational activity spectra of the pyrazine–Au_8 complex under the pre-resonance conditions with the plasmonic excitations of Au_8. The adsorption distance is set to be (a) 4.0 and (b) 10.0 Å. In each figure, the uppermost solid, middle-dotted, and downmost-dotted curves are for the pyrazine-linear Au_8, pyrazine–BOCT Au_8, and the isolated pyrazine, respectively.

2. Massively-Parallel TDDFT Calculations Based on Finite Difference Method in Real-Time and Real-Space

A highly efficient computational 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, the program is highly suitable for massively parallel calculations. Computational performance is severely affected by both increase in network communications and imbalance of CPU time due to waiting for synchronization. These computational bottlenecks are significantly alleviated by utilizing optimal orbital and space hybrid-parallelization procedures. We have achieved electron dynamics simulations with the maximum size of 82,944 nodes (663,552 cores) on the K computer at RIKEN. The peak performance is ~13% with 5,656 nodes and ~10.0% with 22,624 nodes. The method is applied to optical response of arrays of C_{60} orderly nanostructures of more than 10 nm in size. The computed absorption spectrum is in good agreement with the experimental observation.

3. Development of Open-Boundary Cluster Model Approach for Electrochemical Systems and Its Application to Ag^+ Adsorption on Au(111) and Ag(111) Electrodes

We have developed the theoretical method to investigate electrochemical processes by combining OCM with FT-DFT.[3] Introducing OBC rationalized by OCM allows us to well mimic a semi-infinite electrode by using a finite-sized cluster. FT-DFT describes electronic properties in an equilibrium state at a constant μ. The developed method is therefore capable of reproducing the smooth μ dependence intrinsic to semi-infinite systems having the continuous DOS. The conductor-like polarized continuum model named C-PCM is also employed to take account of a solvation effect.

The method is applied to the electrochemical processes of Ag^+ adsorption on the Au(111) and Ag(111) electrodes. The present constant μ approach qualitatively reproduces the experimental evidence that Ag^+ adsorbs more on the Au electrode than the Ag one while the constant N approach gives the opposite result. This result proves that the constant μ condition is absolutely necessary to understand the adsorption. By investigating the relationship between N and μ, it is found that the Au electrode is more negatively charged than the Ag one at any electrode potential because of the difference in their work functions. This is the physicochemical reason for the electrode dependence of the Ag^+ adsorption. The present first-principles method clearly describes such an electrochemical system.

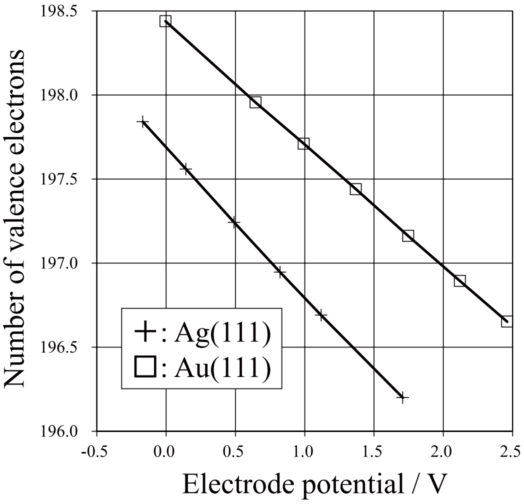

Figure 2. Electrode potential dependence of the number of valence electrons of the Ag(111) (+) and Au(111) (☐) electrodes.

4. Total Structure and Optical Properties of a Phosphine/Thiolate-Protected Au_{24} Nanocluster

This work reports the synthesis and crystal structure determination of a new $[Au_{24}(PPh_3)_{10}(SC_2H_4Ph)_5X_2]^+$ (counterion: X = halide) nanocluster protected by phosphine/ thiolate ligands.[4] This Au_{24} nanocluster exhibits distinct differences from the previously reported Au_{25} nanocluster in the structure and optical properties. DFT calculations reproduced the optical absorption spectrum and interpreted the optical features, which can be divided into high-energy electronic transitions within individual Au_{12} units and a low-energy unique transition due to interactions between two Au_{12} units. The mechanism of preferential growth of $[Au_{24}(PPh_3)_{10}(SC_2H_4Ph)_5X_2]^+$ over $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5X_2]^{2+}$ remains to be unraveled in future work.

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Advanced Electronic Structure Theory in Quantum Chemistry

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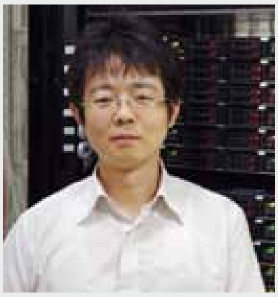

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Quantum chemistry is a subdiscipline of physical chemistry, and practicing its theory by computer is a powerful approach to chemical theory problems that are rather realistic in terms of size and behaviors. We focus on development of the electronic structure theory that is capable of supplying analytic interpretation of chemical phenomena and is being advanced so that it provides accurate information of experiments a priori. The research is aimed at establishing much better ab initio quantum chemistry methodologies that allow one to describe a wide range of complex electronic structures, which can be found in challenging chemical systems, to a predictive chemical accuracy by exploiting cutting-edge many-body theory and sophisticated computing techniques. The resultant methods are applied for studying molecular science.

1. Entangled Quantum Electronic Wave Functions of the Mn_4CaO_5 Cluster in Photosystem II

It is a long-standing goal to understand the reaction mechanisms of catalytic metalloenzymes at an entangled many-electron level, but this is hampered by the exponential complexity of quantum mechanics. Here, by exploiting the special structure of physical quantum states and using the density matrix renormalization group, we compute near-exact many-electron wavefunctions of the Mn_4CaO_5 cluster of photosystem II, with more than 10^{18} quantum degrees of freedom.$^{1)}$ This is the first treatment of photosystem II beyond the single-electron picture of density functional theory. Our calculations support recent modifications to the structure determined by X-ray crystallography. We further identify multiple low-lying energy surfaces associated with the structural distortion seen using X-ray crystallography, highlighting multistate reactivity in the chemistry of the cluster. Direct determination of Mn spin-projections from our wavefunctions suggests that current candidates that have been recently distinguished using parameterized spin models should be reassessed. Through entanglement maps, we reveal rich information contained in the wavefunctions on bonding changes in the cycle (**Figure 1**).

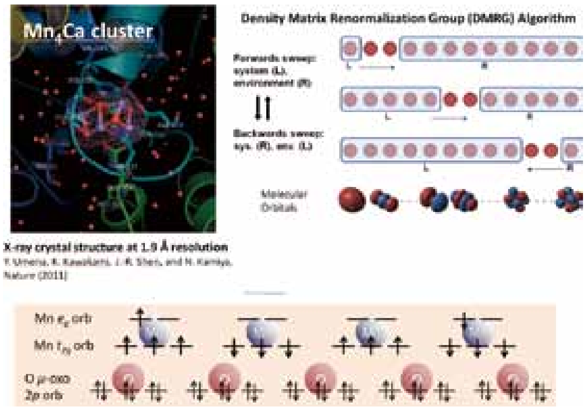

Figure 1. Determination of oxidation state of Mn_4CaO_5 cluster in photosystem II from a multireference wavefunction theory based on Denisty Matrix Renormalization Group method.

The capability to obtain a more controlled description of the electronic structure in this complex problem enabled us to more rigorously address structural and electronic questions for the S1 and S2 states. In the S1 case our work confirms the most recent interpretations, and in the S2 state, our direct access to spin states and spin projections suggests that existing candidates, determined on the basis of agreement with EPR data, must be reassessed. The completeness of the many-electron formulation also allowed us to investigate new phenomenology, for example by computing multiple potential-energy surfaces near the S1 state, which highlight non-adiabaticity and multistate reactivity in the OEC. In addition, we have shown how the information in the many-electron wavefunction can be interpreted through its orbital entanglement map, which graphically illustrates the different kinds of chemical bonding and their changes during the Kok cycle. The detailed mechanistic implications of these changes are intriguing and remain an eventual target of study for the future. More broadly, the theoretical methodology we have established is very generally applicable, and opens up the possibility of understanding the electronic structure and, eventually, the chemical mechanism of biological processes at the entangled quantum many-electron level.

2. Correlated One-Body Potential from Second-Order Møller-Plesset Perturbation Theory: Alternative to Orbital-Optimized MP2 Method

The molecular orbitals (MOs) are a key concept in quantum chemistry to interpret the role of electrons in chemical bondings and reactions. They represent the behavior of one electron moving in the effective potential to which Coulomb interactions with many other electrons are averaged out. The effective mean field description is formulated in the Hartree-Fock (HF) theory as a result of using a single determinant as the model wave function in which electron correlation is dismissed in the solution of many-electron Schrödinger equation. In addition to the shapes of MOs, the orbital energies play a central role to characterize molecular electronic structures. The energy levels and associated canonical MOs are determined as eigenspectrum of the one-electron effective Hamiltonian or the so-called Fock operator that includes the mean field interaction potential.

We have reported the development of a mean-field (or one-particle) theory to represent electron correlation at the level of the second-order Møller-Plesset perturbation (MP2) theory.[2)] Orbitals and associated energy levels are given as eigenfunctions and eigenvalues of the resulting one-body (or Fock-like) MP2 Hamiltonian, respectively. They are optimized in the presence of MP2-level correlation with the self-consistent field procedure and used to update the MP1 amplitudes including their denominators. Numerical performance is illustrated in molecular applications for computing reaction energies, applying Koopmans' theorem, and examining the effects of dynamic correlation on energy levels of metal complexes.

3. Multireference Configuration Interaction Theory Using Cumulant Reconstruction with Internal Contraction of Density Matrix Renormalization Group Wave Function

We report development of the multireference configuration interaction (MRCI) method that can use active space scalable to much larger size references than has previously been possible[3)] (**Figure 1**).The recent development of the density matrix renormalization group (DMRG) method in multireference quantum chemistry offers the ability to describe static correlation in a large active space. The present MRCI method provides a critical correction to the DMRG reference by including high-level dynamic correlation through the CI treatment. When the DMRG and MRCI theories are combined (DMRG-MRCI), the full internal contraction of the reference in the MRCI ansatz, including contraction of semi-internal states, plays a central role. However, it is thought to involve formidable complexity because of the presence of the five-particle rank reduced-density matrix (RDM) in the Hamiltonian matrix elements. To address this complexity, we express the Hamiltonian matrix using commutators, which allows the five-particle rank RDM to be canceled out without any approximation. Then we introduce an approximation to the four-particle rank RDM by using a cumulant reconstruction from lower-particle rank RDMs. A computer-aided approach is employed to derive the exceedingly complex equations of the MRCI in tensor-contracted form and to implement them into an efficient parallel computer code. This approach extends to the size-consistency-corrected variants of MRCI, such as the MRCI+Q, MR-ACPF, and MR-AQCC methods. We demonstrate the capability of the DMRG-MRCI method in several benchmark applications, including the evaluation of single-triplet gap of free-base porphyrin using 24 active orbitals.

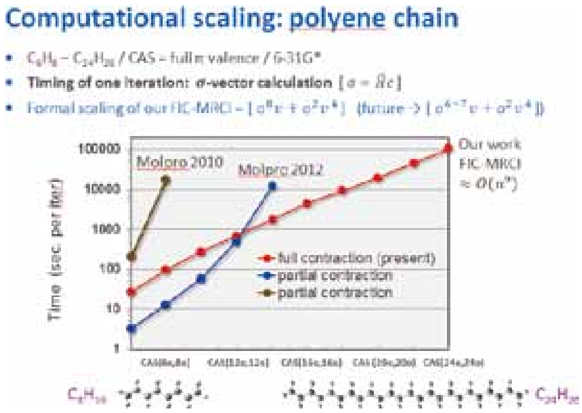

Figure 2. Calculation times (in seconds) of a single iteration including the construction of a σ vector in FIC-cu(4)-, CW-, WK-MRCI calculations for polyene molecules from C_6H_8 to $C_{24}H_{26}$ with the CAS(*ne*,*no*) reference.

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Award

YANAI, Takeshi; The 2013 International Academy of Quantum Molecular Science Medal.

Theoretical Study on Photochemistry and Catalysis

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We investigate the photochemistry or photophysical properties of molecules based on the accurate coupled cluster methodologies, that are of interest in view of fundamental chemistry or material chemistry. We also focus on the mechanism and theoretical design of the various types of catalytic reactions on nanoparticles or bulk surface by developing the theoretical approaches of hetero junction. In this report, we present our recent studies on the mechanism for solvatochromic shifts of free-base porphine,1) electronic excitations of C_{60} fullerene,2) theoretical design of dye-sensitized solar cells,3) and interatomic relaxation effects of double core hole states.

1. Mechanism for Solvatochromic Shifts of Free-Base Porphine

It has been known that π–π* excitation energies of nonpolar conjugated molecules generally exhibit a bathochromic shift (redshift) in solution. The origin of this bathochromic shift is considered to be the dispersive interaction between solute and solvent molecules. Several studies have been conducted on the mechanisms of the solvatichrimic shift for nonpolar molecules, and many models have been proposed. However, different approximations lead different conclusions. The dispersive interaction in excited electronic states has not yet been well understood.

The solvatochromic shifts of free-base porphine in the Q- and B-bands were studied using the polarizable continuum model (PCM) and explicit solvent molecules employing TDDFT and the SAC-CI method. The state-specific and linear-response methods were examined in the PCM calculations. These methods involve different types of solute–solvent interactions. The SAC-CI calculation with explicit solvent molecules includes all types of microscopic solute–solvent interactions including dispersive interaction. Based on our calculations the experimental trends in the solvatochromic shifts of free-base porphine can be explained as follows.

1. The observed bathochromic shift of the B-band in solution is attributed to the interaction of transition dipole with the solvent reaction field.
2. The dispersive interaction caused by the polarizability difference between the ground and excited states is an origin of the observed decrease in the Q-band splitting in nonpolar solvents.
3. The observed refractive index-dependence of the solvent shift in n-alkane can be explained by the dispersive interaction, which relate to the optical dielectric constants of bulk solvent
4. The remarkable decrease in the Q-band splitting in dipolar and quadrupolar solvents cannot be explained by the dispersive interaction alone. Specific solute–solvent interactions are important. Anisotropic interactions are more important than the geometry relaxation for the decrease in the Q-band splitting in solution.

2. Electronic Excitations of C_{60} Fullerene

Because of its unique photo-electronic properties, C_{60} fullerene well known as buckyball, is receiving an extensive interest in terms of scientific and practical purposes. Derivatives of C_{60} are expected to be practical materials for organic thin-film solar cells. Their electronic structure is, however, quite complicated; it is highly-degenerated and delocalized. Therefore, it has been difficult to perform quantum chemical calculations for excited states of C_{60} fullerene using highly accurate theories. We successfully applied the direct SAC-CI method to C_{60} fullerene. The excited states of C_{60} were accurately calculated by the direct SAC-CI method in the visible to near UV region (below 6.2 eV, 200 nm).

Figure 1 shows the comparison between the SAC-CI results and experimental spectrum of C_{60}, where circles and x-marks denote optically-forbidden states by the selection rule. The absorption in 500–600 nm corresponds to optically-forbidden states, and therefore, very weak absorption peaks are observed induced by vibronic couplings.

The assignments of photoabsorption spectrum based on the direct SAC-CI results are partially different from the previous assignments based on the semi-empirical molecular orbital calculations. In the previous study, the band A observed around 400 nm has been assigned to the optically-allowed 1^1T_{1u} state; based on the direct SAC-CI calculations, however, this peak should be assigned to the optically-forbidden 1^1T_{2u} state. The present assignment based on the direct SAC-CI results can explain the experimental findings more consistently than the previous study.

To understand the electronic excited states of fullerenes and to predict their energetics are essentially important for the development of molecular electronics such as organic thin-film solar cells. For such purpose, semi-empirical molecular orbital method and density functional theory are insufficient. It is necessary to use highly accurate wavefunction theories that are applicable to large systems such as the direct SAC-CI method.

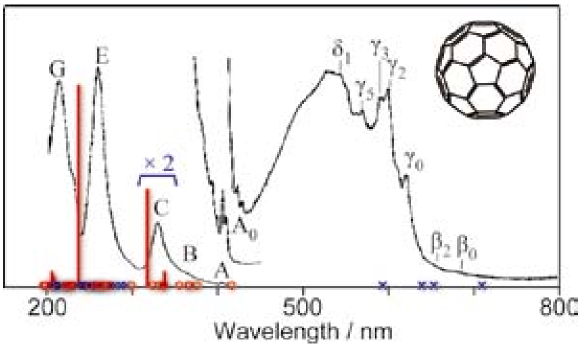

Figure 1. The SAC-CI results and experimental absorption spectrum of C_{60} fullerene.

3. Theoretical Study on Dye-Sensitized Solar Cells (DSSCs)

Dye-sensitized solar cell (DSSC) is a solar battery using cheap metal oxides like titanium oxide (TiO_2). It is expected as a low-cost solar battery without using the silicon semiconductor. Because TiO_2 does not have photoabsorption in the visible region, the organic dyes adsorbed on the titanium oxide is used as a sensitizer and the electromotive force and electric current are achieved by the electron transfer from the electronically excited dyes to TiO_2. Because many factors concern to the efficiency and durability of the cells, the design based on the quantum chemical calculations is necessary. The D-D-π-type organic dyes with two electron donors (D), π-spacer (π), and acceptor (A) suggested by experiment show relatively high energy conversion efficiency. We obtained detailed assignments of the excited states, stability, and assembly of these dyes by theoretical calculations. In addition, the electronic injection process to TiO_2 conduction band was calculated using a cluster model. "Direct" mechanism where the electron injection from dyes to TiO_2 occurs directly was suggested by calculations and the high efficiency of electron injection was supported theoretically.

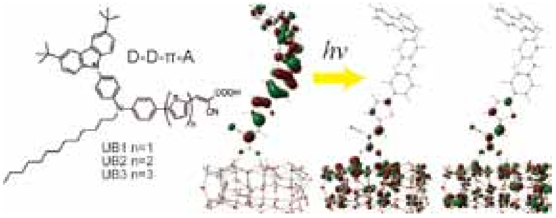

Figure 2. Structure of the D-D-π-type DSSC and direct mechanism. Electronic transition occurs from the dye MO to TiO_2 conduction band.

4. Polarization and Site Dependence of Interatomic Relaxation Effects in Double Dore Hole States

The interatomic relaxation (IR) effects of two-site double core hole (tsDCH) states in selected molecules with a polarizable unit have been systematically investigated using *ab initio* calculations. The IR effects are analyzed by varying size of this polarizable unit and its position relative to the DCHs. The systems with the DCHs located at the opposite sides of the polarizable unit show large negative IR energies, while those at the same side of the polarizable unit have smaller negative IR effects. Here, the IR energies can even be positive if the polarizable unit is large enough. The generalized Wagner plots of tsDCH states are used to visualize the trend of the IR effects in the molecules studied.

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Development of New Algorithms for Molecular Dynamics Simulation and Its Application to Biomolecular Systems

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Biomolecules such as proteins and peptides have complicated free-energy landscape with many local minima. In the conventional canonical-ensemble simulations, it is difficult to realize efficient samplings in such systems because the 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 helix-strand replica-exchange method and replica- permutation method. It is important to realize efficient samplings in the conformational space and to predict the native structures of proteins. We apply these methods to proteins and peptides.

1. Transformation of a Design Peptide between the α-Helix and β-Hairpin Structures by a Helix-Strand Replica-Exchange Molecular Dynamics Simulation

We investigated the transformation between the α-helix and β-hairpin structures of an 18-residue design peptide, whose sequence is INYWLAHAKAGYIVHWTA.[1] This peptide has both α-helix and β-hairpin structures in aqueous solution. For this purpose, we proposed the helix-strand replica-exchange method. This is one of the Hamiltonian replica-exchange methods in which we exchange parameters for umbrella potentials to enhance the α-helix or β-strand structure formation, as in Figure 1. We performed an all-atom helix-strand replica-exchange molecular dynamics (MD) simulation of this peptide in explicit water solvent with five replicas. Because the suitable umbrella potential was applied, the helix-strand replica-exchange MD simulation reproduced conformations closer to experimental conformations than a temperature replica-exchange MD simulation when the same numbers of the replicas were used, while the temperature replica-exchange MD simulation does not require bias along any specific order parameter. We calculated its free-energy landscape and revealed the transformation pathways between the α-helix and β-hairpin structures and the folding pathways from an extended structure. The free-energy difference between the two structures is calculated to be almost zero, which agrees with the experimental results.

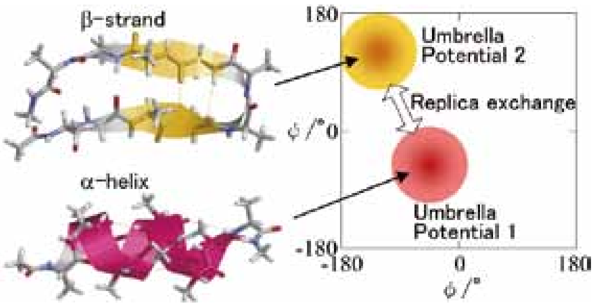

Figure 1. Schematic illustration of the helix-strand replica-exchange method.

2. Replica-Permutation Method with the Suwa-Todo Algorithm beyond the Replica-Exchange Method

We proposed a new method for MD and Monte Carlo simulations, which is referred to as the replica-permutation method, to realize more efficient sampling than the replica-exchange method.[2] In replica-permutation method, not only exchanges between two replicas but also permutations among more than two replicas are performed, as in Figure 2. Furthermore, instead of the Metropolis algorithm, the Suwa–Todo algorithm is employed for replica-permutation trials to minimize its rejection ratio. We applied RPM to particles in a double-well potential energy, Met-enkephalin in a vacuum, and a C-peptide analog of ribonuclease A in explicit water. For comparison purposes, replica-exchange molecular dynamics simulations were also performed. As a result, replica-permutation method sampled not only the temperature space but also the conformational space more efficiently than REM for all systems. From our simulations of C-peptide, we obtained the α-helix structure with salt bridges between Gly2 and Arg10, which is known in experiments. Calculating its free-energy landscape, the folding pathway was revealed from an extended structure to the α-helix structure with the salt bridges.

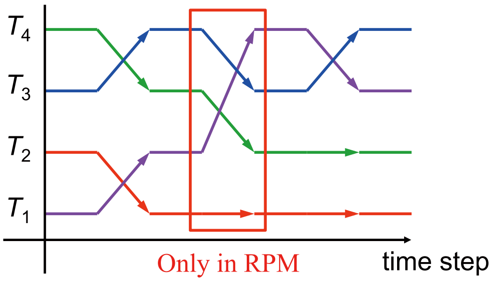

Figure 2. An example of time series of temperatures in replica-permutation method (RPM). The transitions of replicas in the red square frame are not realized in replica-exchange method (REM).

3. Pressure-Induced Helical Structure of a Peptide Studied by Simulated Tempering Molecular Dynamics Simulations

It is known experimentally that an AK16 peptide forms more α-helix structures with increasing pressure while proteins unfold in general. In order to understand this abnormality, MD simulations with the simulated tempering method for the isobaric–isothermal ensemble were performed in a wide pressure range from 1.0 × 10^{-4} GPa to 1.4 GPa.3) From the results of the simulations, it is found that the fraction of the folded state decreases once and increases after that with increasing pressure. The partial molar volume change from the folded state to unfolded state increases monotonically from a negative value to a positive value with pressure. The behavior under high pressure conditions is consistent with the experimental results. The radius of gyration of highly helical structures decreases with increasing pressure, which indicates that the helix structure shrinks with pressure. This is the reason why the fraction of the folded state increases as pressure increases.

4. Decomposition-Order Effects of Time-Integrator on Ensemble Averages for the Nosé-Hoover Thermostat

Decomposition-order dependence of time development integrator on ensemble averages for the Nosé-Hoover dynamics is discussed.4) Six integrators were employed for comparison, which were extensions of the velocity-Verlet or position-Verlet algorithm. Molecular dynamics simulations by these integrators were performed for liquid-argon systems with several different time steps and system sizes. The obtained ensemble averages of temperature and potential energy were shifted from correct values depending on the integrators. These shifts increased in proportion to the square of the time step. Furthermore, the shifts could not be removed by increasing the number of argon atoms. We show the origin of these ensemble-average shifts analytically. Our discussion can be applied not only to the liquid-argon system but also to all MD simulations with the Nosé-Hoover thermostat. Our recommended integrators among the six integrators are presented to obtain correct ensemble averages.

5. Cutoff Effect in the Nosé-Poincaré and Nosé-Hoover Thermostats

We performed MD simulations of a Lennard-Jones system and investigated the effect of potential cutoff in the Nosé–Poincaré and Nosé–Hoover thermostats.5) The Nosé–Poincaré thermostat is the symplectic algorithm of the Nosé thermostat, while the Nosé–Hoover thermostat is not a symplectic algorithm. If the potential energy is twice or more differentiable, the Hamiltonian was conserved well in the Nosé–Poincaré thermostat. If the potential energy is once or less differentiable, however, the Hamiltonian was not conserved, but increased because the continuity of potential energy is required in a symplectic MD simulation. The increase in the Hamiltonian caused the increase in instantaneous temperature, and physical quantities cannot be obtained correctly. It is because the difference in the Hamiltonian effectively increases the set temperature in the equations of motion. On the other hand, the Hamiltonian was not conserved for any cutoff method in the Nosé–Hoover thermostat because it is not a symplectic algorithm. However, temperature was controlled appropriately because the Hamiltonian deviation does not affect the set temperature.

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Theory and Computation of Reactions and Properties in Solutions and Liquids

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

ISHIDA, Tateki
Assistant Professor

We 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 focuses on 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 with molecular dynamics simulation.

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

We have developed a procedure for tracking 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 prescription for studying electron energy transfer processes in the excited state in solution. It is revealed that the coupling between solvation dynamics and a fast intramolecular electron energy transfer is likely to play an important role in the emergence of photoinduced unique functionalities in biochemical and metal complex systems.

2. Investigations of Dynamical Properties on Ionic Liquids$^{1–2)}$

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

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Visiting Professors

Visiting Professor

HASEGAWA, Jun-ya *(from Hokkaido University)*

Quantum Chemistry for the Excited States of Functional Molecules in Proteins and Solutions

Molecular interactions between chromophore and environment are the essential to furnish a protein with the photo-functionality. I am interested in the machinery of the photo-functions such as photo-synthesis, vision, and bioluminescence. To understand the mechanism and to develop chemical concept behind the photo-functions, we develop electronic structure theories for excited state, analytical method for excitation-energy transfer pathway, and a hybrid quantum-mechanics/molecular mechanics method. In recent studies, we have clarified color-tuning mechanism of photo-functional proteins and excitation transfer mechanism of bridge-mediated donor-acceptor systems. We are also interested in developing a configuration interaction picture for the solvatochromic response of the molecular environment.

Visiting Associate Professor

ANDO, Koji *(from Kyoto University)*

Quantum Transfer Processes in Chemical and Biological Systems

At the core of chemistry, biochemistry, and materials sciences are reduction-oxidation and acid-base reactions, in which electron and proton transfers are the key elementary processes. Our research group has been working on theoretical and computational modeling of these inherently quantum dynamical processes in condensed matters. One recent achievement is a development of new quantum Monte Carlo simulation method with an account of induced-dipole corrections obtained from fragment molecular orbital calculations. It adequately described isotope mixing effect of dielectric phase transition temperature of hydrogen-bonding organic molecular crystal. Another is a development and numerical assessment of initial-value-represented propagator for semiquantal squeezed-state wave packet propagation, which extends our previous works of nuclear wave packet molecular dynamics simulation method.

Visiting Associate Professor

MORISHITA, Tetsuya *(from AIST)*

Development of *ab initio* Mean-Force Dynamics for Free-Energy Calculations

We have been developing a method for constructing free-energy profiles in the framework of *ab initio* molecular-dynamics. It is well known that the electronic state needs to be explicitly taken into account to describe bond formation or bond breaking in. *e.g.*, conformational transformations of biomolecules, which plays an important role in constructing their free-energy profiles. Developing force-fields that can describe such bond formations is, however, considered to be extremely difficult. It is therefore of great importance to develop a method that enables us to construct free-energy profiles without empirical force-fields.

Our interest particularly focuses on the incorporation of *ab initio* interatomic interactions into logarithmic mean-force dynamics (LogMFD), which is expected to enable us to efficiently construct free-energy profiles within the accuracy of *ab initio* force-fields. A preliminary result of “*ab initio*” LogMFD calculation for glycine dipeptide molecule has been recently obtained. We found that the free-energy landscape is sensitive to the description of the hydrogen bonding, which may not be appropriately handled with an empirical force-field only.