RESEARCH ACTIVITIES I
Department of Theoretical Studies

I-A Development of New Numerical Techniques in the Study of Molecular Structure

Although theories of the electronic structure of molecules have been extensively developed for last decades, almost always new methods and techniques have to be developed to meet new experimental advances.

I-A-1 Spectral Density Calculation by Using the Chebyshev Expansion

IKEGAMI, Tsutomu; IWATA, Suehiro

A method to calculate the spectral density of any state vectors with respect to a set of eigenstates of a Hamiltonian is proposed. An expectation value of a spectral density operator, $\delta(H\text{-}E)$, gives the spectral density of the state vector. The operator is evaluated by using the Chebyshev expansion method without the diagonalization procedure for the Hamiltonian. Two expansion schemes are examined. The one is the direct expansion, where the delta function is expanded in the Chebyshev polynomials. This scheme is simple and efficient, though it is difficult to guarantee the convergence of the expansion, especially for a bound system. The other is the indirect expansion, where the expansion is performed in the Fourier space. Here, the convergence is guaranteed, independently of the energy spectrum of the Hamiltonian. This scheme is identical in the spirit to Heller's autocorrelation function method, though the explicit time propagation of the wavepacket is avoided. Because of this, a spectral transformation function is naturally introduced to improve resolution at the low energy region.

I-A-2 Calculation of the ZEKE Spectrum of CO

IKEGAMI, Tsutomu; IWATA, Suehiro

The ZEKE spectrum of CO is calculated by using the spectral density method. The ab initio potential energy curves of the excited states of CO^+, calculated by Okada and Iwata, are fitted to the two states model (2×2 matrix). The diagonal part is fitted well with the Morse functions and the off-diagonal is assumed to constant. The centrifugal part (Hund's case a) is added to obtain the rot-electronic potential curves. The Gaussian wavepacket, corresponding to the vibrational wavefunction of the ground state of CO, is placed on the coupled potential energy curves, and its spectral density is calculated. A series of the vibrational predissociation spectra of CO^+ is thus obtained for several rotational states. They are superimposed to obtain the rot-vibrational spectrum. The rotational line strengths for the photoionization process are calculated based on the BOS model,[1] borrowing the coefficients from the experimental result by Shiell *et al.*[2] The results are shown in Figure 1. The line widths for $v = 3$ and 4, whose levels are above the avoided crossing, are broad due to the short lifetime of the states. However, the line width for $v = 5$ becomes narrow again. By using Zhu-Nakamura's theory, it was found that the perfect reflection condition at the avoided crossing is met for the energy level of $v = 5$, which results in the long lifetime of the state.

References

1) A. D. Buckingham, B. J. Orr and J. M. Sichel, *Philos. Trans. R. Soc. London*, Ser. A 268, 147 (1970).
2) R. C. Shiell, M. Evans, S. Stimson, C.-W. Hsu, C. Y. Ng and J. W. Hepburn, *Chem. Phys. Lett.* **315**, 390 (1999).

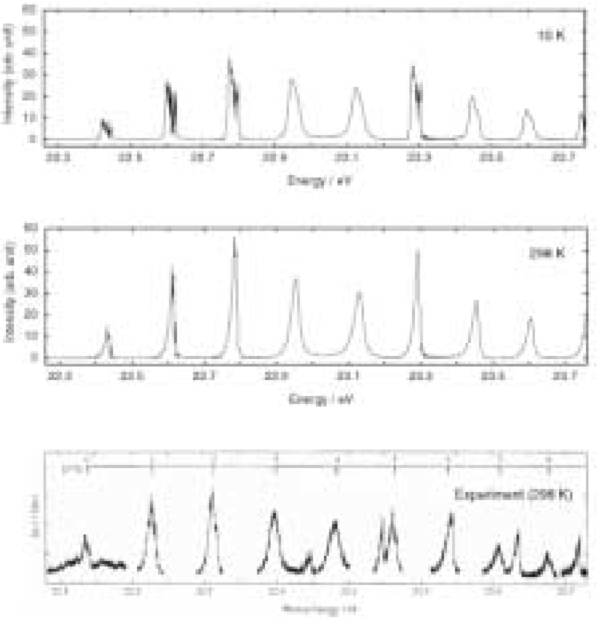


Figure 1. Calculated and experimental ZEKE spectra of CO.

I-A-3 Nonadiabatic Relaxation Through a Conical Intersection

IKEGAMI, Tsutomu; IWATA, Suehiro

Nonadiabatic relaxation process is studied on two dimensions-two levels system with a conical intersection. The upper potential energy surface is concave around the conical intersection, while the nonadiabatic coupling is increased to infinity at the intersection. From a classical point of view, the trajectory running on the upper surface with less kinetic energy is more attracted to the conical intersection, and hence the nonadiabatic transition to the lower surface is expected to occur more frequently. This dependence of the transition probability is qualitatively different from the one-dimension system, where all the trajectories pass the same line independent of the kinetic energy. The above classical picture is examined quantum mechanically by using the wavepacket propagation method. The Gaussian wavepacket is placed behind the conical intersection, and is injected toward the intersection with several kinetic energies. The parameters of the model are tuned to simulate typical photochemical processes. As expected, the more fractions of the wavepacket stay on the upper surface with the increase of the injection energy. The destructive interference can also be observed on the upper surface, which is due to the Berry's phase, if the system setup is taken to be symmetric.

I-B Electron-Hydrogen Bond in Water Clusters and Their Complexes with Atomic Ions

While we have been studying water cluster anions $(H_2O)_n^-$, we have found a unique structural unit in which the OH bonds surround an excess electron. We call it OH{e}HO structure. This structure is also found in the water cluster complexes with a group 1 metal atom. The correlation between the HO bond lengthening and the downward shift of HO stretching harmonic frequency in the OH{e}HO structure is almost identical with that in the ordinal hydrogen bond. Because of that, we call the interaction electron-hydrogen bond. In addition to the vibrational spectroscopy, we theoretically examine the electronic absorption spectra, which hopefully help to identify the isomers of the clusters.

I-B-1 Theoretical Studies of the Water-Cluster Anions Containing the OH{e}HO Structure: Energies and Harmonic Frequencies

TSURUSAWA, Takeshi; IWATA, Suehiro

[*Chem. Phys. Lett.* **315**, 433 (2000)]

In addition to isomers having a dipole-bound electron, the internal bound isomers of trimer, tetramer and hexamer water anions are found using ab initio MO calculations. The internal bound isomers have a characteristic OH{e}HO structure. The interaction between the excess electron {e} and the surrounding OH bonds holds the structure stable. The calculated vibrational infrafed spectrum for a hexamer anion with two double proton-acceptor water molecules shows a qualitatively similar vibrational spectrum with the one observed by Johnson and his coworkers. A strong correlation between the vertical detachment energy and the distribution of the excess electron is also found.

I-B-2 Electron-Hydrogen Bonds and OH Harmonic Frequency Shifts in Water Cluster Complexes with a Group 1 Metal Atom, $M(H_2O)_n$ (M = Li and Na)

TSURUSAWA, Takeshi; IWATA, Suehiro

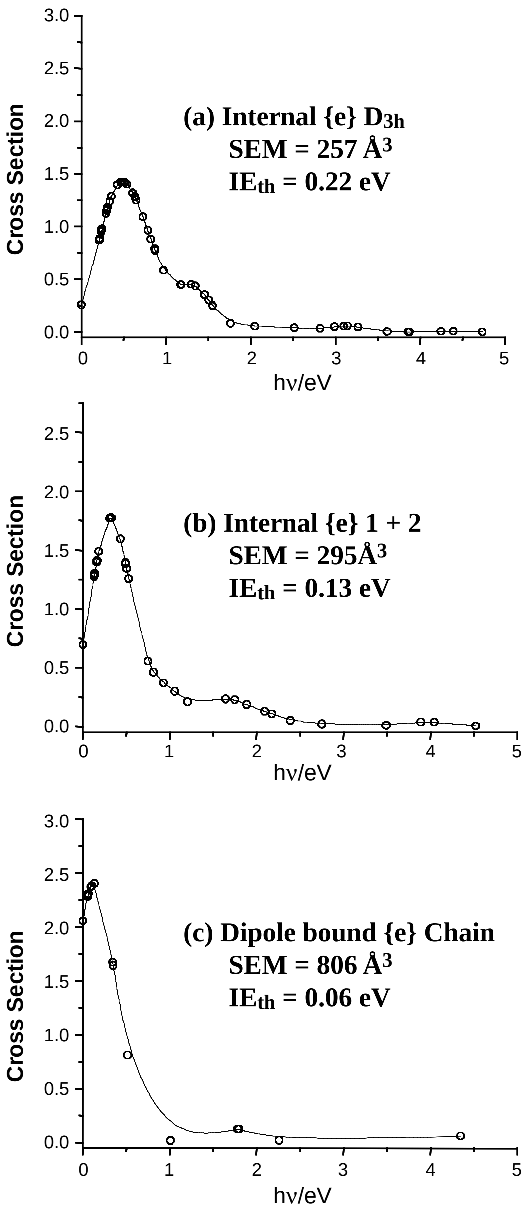
[*J. Chem. Phys.* **112**, 5705 (2000)]

The harmonic vibrational frequencies for $M(H_2O)_n$ (M = Li and Na) are calculated with ab initio MO methods. Three types of isomers, surface, quasi-valence and semi-internal, exhibit the characteristic frequency shifts $\Delta\nu_{OH}$. The calculated spectral patterns are related to the geometric conformations around the localized electron {e} in the cluster. The downward shifts of OH frequencies are strongly correlated with the lengthening of OH bond distances, as is well known in the hydrogen bonds. The magnitude of the downward shift is as large as that for the hydrogen bond. The correlation of the shifts with the distance between the center of the electron {e} and the hydrogen atom reveals two types of interaction schemes. The characteristics of the structural unit OH{e}HO in $M(H_2O)_n$ and its OH modes are common with those found in water anion clusters. The interaction between the localized electron and OH bonds can be called electron-hydrogen bond.

I-B-3 Theoretical Study of Photoabsorption Cross Sections of Water Cluster Anions

CHEN, Fei-Wu[1]; TSURUSAWA, Takeshi; IWATA, Suehiro
([1]JST)

Photoabsorption cross sections of water dimer and trimer anions are calculated with an ab initio molecular orbital method. Because the electron detachment energy of these small water cluster anions is less than 0.3 eV, all of the photoabsorption spectra in the near infrared and visible region are due to the bound-free transitions. To construct the bound-free continuum spectrum, the L^2 integrable method is used with the single reference polarization configuration interaction (POL CI) method. The convergence on the basis set is examined by adding diffuse functions. Two isomers of dimer anion and three isomers of trimer anion are studied. The calculated photoabsorption spectra of three trimer anions are shown in Figure. The spectra was drawn from the vertical ionization energy IE_{th}, which is given in the figure along with SEM; SEM is the volume of the excess electron distribution containing a half of the electron. The spectrum of isomer of dipole bound electron (c) is different from those of the isomers of internally trapped electron.



I-B-4 Theoretical Study of Photoabsorption Spectra of $M(H_2O)_n$ (M = Li and Na)

IWATA, Suehiro[1]; CHEN, Fei-Wu[2]; TSURUSAWA, Takeshi
([1]IMS and Hiroshima Univ.; [2]JST)

By examining the electron distribution of the singly occupied orbital (SOMO) of $M(H_2O)_n$ (M = Li and Na) of several isomers, we have shown that most of isomers of $n = 3$ and 4 and all of isomers of $n > 4$ are the ion pair complexes $M^+(H_2O)_n^-$ (*J. Phys. Chem. A* **103**, 6134 (1999)). To characterize the electronic structure of the complexes, the photoabsorption spectrum is theoretically constructed with ab initio MO calculations of single-excitation level of approximation (SCI). In $n =$ 1 and 2, the lowest transitions are the intra-valent $s \rightarrow p$ transitions, while in the ion-pair complexes, the lowest transitions are of back-charge transfer to the metal's s and p orbitals from the trapped electron in the OH{e}HO structure. Notably, below the ionization threshold, which is about 3.5 eV, many but weak Rydberg type transitions are predicted.

I-C Computational Chemistry of Atomic and Molecular Processes in Atmospheric Environment

In 1998 we launched a new research project, "Computational Chemistry for Atmospheric Environmental Molecule" under Research and Development Applying Advance Computational Science and Technology administrated by Japan Science and Technology Corporation (ACT-JST). The atmospheres on the earth as well as on the sun and on planets consist of simple molecules, for which we can now perform the state-of-art calculations from the first principle of quantum mechanics. The calculated molecular physical properties such as spectroscopic constants are accurate enough to be used as "the experimental data." Moreover, physical and chemical phenomena in the atmosphere sometimes involve a sequence of complex processes. To explore the processes, development of new theoretical methods might be required, based both on classical and quantum theories.

I-C-1 Accurate Potential Energy and Transition Dipole Moment Curves for Several Electronic States of CO^+

OKADA, Kazutoshi[1]; IWATA, Suehiro
([1]GUAS)

[*J. Chem. Phys.* **112**, 1804 (2000)]

Accurate calculations were performed for several doublet and quartet states of CO^+ using the multi-reference configuration interaction method. With a single set of molecular orbitals the accurate transition dipole moments were evaluated. The calculated lifetimes of the vibronic states of the $A^2\Pi$ and $B^2\Sigma^+$ states were in excellent agreement with the available experimental data. The calculated vibrational level spacings and rotational constants up to v = 40 of the $^2\Sigma^+$ state were compared with the latest experimental data, and quantitative agreement was attained.

I-C-2 Ab initio MO Study of the *A*, *D* and Third $^2\Pi$ States of CO^+

OKADA, Kazutoshi[1]; IWATA, Suehiro
([1]GUAS)

[*J. Electron. Spectrosc. Relat. Phenom.* **108**, 225 (2000)]

Ab initio MO calculations were performed for three $^2\Pi$ states of CO^+ with the multi-reference configuration interaction method. Spectroscopic constants were evaluated also for other low-lying states. For the $^2\Sigma^+$ state, $A^2\Pi$, and $B^2\Sigma^+$ states, the calculated spectroscopic constants are in very good agreement with experimental data within the limit of experimental accuracy. In the photoelectron spectra, a series of the vibrational progression assigned to the $D^2\Pi$ state persists up to v = 9, whereas the calculated adiabatic potential energy holds only three vibrational levels below a barrier at R = 1.44 Å, which results from an avoided crossing with the upper state, third $^2\Pi$. The observed progression was analyzed in terms of the resonant states obtained from the coupling of two strongly interacting diabatic states, second and third $^2\Pi$.

I-C-3 Theoretical Studies of Einstein's *A* and *B* Coefficients of Rovibrational Transitions for Carbon Monoxide: Simulation of Temperature Distribution of CO in the Solar Atmosphere

OKADA, Kazutoshi[1]; AOYAGI, Mutsumi; IWATA, Suehiro
([1]GUAS and JST)

Accurate calculations of potential energy and dipole moment curves were performed for the ground state of CO with the multi-reference configuration interaction method. Vibrational and spectroscopic constants were evaluated. Rovibrational levels on the potential energy curve were obtained. Transition intensities between rovibrational levels were obtained by accurately evaluating Einstein's *A* and *B* coefficients under an assumption of the thermal distribution among the rovibronic levels. We successfully simulated the infrared absorption spectra observed on a satellite of NASA in the atmosphere of the Sun. The comparison of the simulated spectrum for the Δv = 2 transitions with the observed spectrum indicates that carbon monoxide molecules in the sun atmosphere are distributed in the temperature range of 5000–5500 K.

I-C-4 Theoretical Study on the Hydrogen Abstraction from Saturated Hydrocarbons by OH Radical

HASHIMOTO, Tomohiro[1]; IWATA, Suehiro
([1]JST)

Weakly-bound reactant and product complexes in the hydrogen abstraction by OH radical from CH_4, C_2H_6, and C_3H_8 are investigated using ab initio molecular orbital methods. Calculated binding energies of CH4 and OH reactant complex at CCSD(T)/aug-cc-pVTZ (aug-cc-pVDZ) levels are 0.54 (0.74) kcal/mol. Including zero-point vibrational energy corrections at MP2 level with the corresponding basis sets reduce the binding energies to 0.16 (0.08) kcal/mol which are much smaller than the experimental estimation (about 0.60 kcal/mol). Product complex for the CH_4 + OH system, which is more stable than the reactant complex, has the binding energies of 0.77 (0.79) kcal/mol at CCSD(T)/aug-cc-pVTZ (aug-cc-pVDZ) levels with MP2 zero-point energy corrections. The reactant and product complexes are also found for C_2H_6 + OH and C_3H_8 + OH systems at CCSD(T)/aug-cc-pVDZ level of theory. These binding energies have a tendency to get larger as the number of carbon atom increases.

I-C-5 Theoretical Study on the Reaction Mechanism for Oxidation of Isoprene

AMMAL, S. Salai Cheettu[1]; HASHIMOTO, Tomohiro[1]; IWATA, Suehiro
([1]JST)

The reaction of OH radical with isoprene molecule followed by the addition of O_2 molecule to form the peoxy radicals were studied by ab initio molecular orbital methods. The equilibrium geometries and vibrational frequencies were determined for all reactants, products, and transition states, as well as activation and reaction energies. Geometries were obtained at the UHF and UMP2/cc-pVDZ levels while energies were computed at UMP4, PMP2, and PMP4 levels. The addition of OH radical to the terminal carbon atoms of isoprene molecule are found to be more favorable in the first step of the reaction, whereas the radicals obtained by the addition of OH at the two inner carbon atoms are found to have lower activation barriers for the addition of O_2 molecule in the second step of the reaction. The six peroxy radicals obtained are much closer in stability and among them the radicals possessing the OH and OO· groups at the neighboring carbon atoms are found to be more stable.

I-D Prediction of Protein Tertiary Structures from the First Principles

Prediction of the three-dimensional structures of protein molecules by computer simulations is a very challenging problem in theoretical molecular science. The difficulty of the problem lies in two facts: (1) the inclusion of accurate solvent effects is non-trivial and time-consuming (2) there exist huge number of local minima in the energy function, forcing conventional simulations to get trapped in states of energy local minima. We have been exploring the strategies that allow us to overcome these difficulties.

I-D-1 Helix-Coil Transitions of Amino-Acid Homo-Oligomers in Aqueous Solution Studied by Multicanonical Simulations

MITSUTAKE, Ayori; OKAMOTO, Yuko

[*J. Chem. Phys.* **112**, 10638 (2000)]

Helix-coil transitions of homo-oligomers in aqueous solution are studied by multicanonical Monte Carlo simulations. The solvation effects are represented by the sum of the terms that are proportional to the solvent-accessible surface area of the atomic groups. Homo-oligomers of length 10 are considered for three characteristic amino acids, alanine, valine, and glycine, which are helix former, helix indifferent, and helix breaker, respectively. We calculated as a function of temperature the distributions of the backbone dihedral angles, the average values of total energy, and its component terms of the homo-oligomers. It is shown that for homo-alanine the helix-coil transition exists and that the transition temperature in water is considerably lower than in gas phase, which implies that the effects of solvation tend to reduce helical content. Moreover, the helix propagation parameter s and nucleation parameter σ of the Zimm-Bragg model were calculated. The s values that were obtained from the simulations in aqueous solution are in remarkable agreement with the experimental results.

I-D-2 Multidimensional Replica-Exchange Method for Free Energy Calculations

SUGITA, Yuji; KITAO, Akio[1]; OKAMOTO, Yuko
([1]Kyoto Univ.)

[*J. Chem. Phys.* **113**, 6042 (2000)]

We have developed a new simulation algorithm for free energy calculations. The method is a multidimensional extension of the replica-exchange method. While pairs of replicas with different temperatures are exchanged during the simulation in the originalreplica-exchange method, pairs of replicas with different temperatures and/ or different parameters of the potential energy are exchanged in the new algorithm. This greatly enhances the sampling of the conformational space and allows accurate calculations of free energy in a wide temperature range from a single simulation run, using theweighted histogram analysis method.

I-D-3 Replica-Exchange Multicanonical Algorithm and Multicanonical Replica-Exchange Method for Simulating Systems with Rough Energy Landscape

SUGITA, Yuji; OKAMOTO, Yuko

[*Chem. Phys. Lett.* **329**, 261 (2000)]

We propose two efficient algorithms for configurational sampling of systems with rough energy landscape. The first one is a new method for the determination of the multicanonical weight factor. In this method a short replica-exchange simulation is performed and the multicanonical weight factor is obtained by the multiple-histogram reweighting techniques. The second one is a further extension of the first in which a replica-exchange multicanonical simulation is performed with a small number of replicas. These new algorithms are particularly useful for studying the protein folding problem.

I-D-4 Multicanonical Algorithm Combined with the RISM Theory for Simulating Peptides in Aqueous Solution

MITSUTAKE, Ayori; KINOSHITA, Masahiro[1]; OKAMOTO, Yuko; HIRATA, Fumio
([1]Kyoto Univ.)

[*Chem. Phys. Lett.* **329**, 295 (2000)]

This letter contributes to the development of the first-principles prediction methods for peptide and protein conformations in aqueous solution. We report results of the first attempt to combine the multicanonical algorithm for extensive sampling of the phase space and the reference interaction site model theory for incorporating solvent effects. Met-enkephalin in aqueous solution is chosen as an example system. Averages of the energy functions, end-to-end distance, and dihedral-angle distributions are calculated as functions of temperature.

I-D-5 A pH-dependent Variation in α-Helix Structure of the S-peptide of Ribonuclease A Studied by Monte Carlo Simulated Annealing

NAKAZAWA, Takashi[1]; BAN, Sumiko[1]; OKUDA, Yuka[1]; MASUYA, Masato[2]; MITSUTAKE, Ayori; OKAMOTO, Yuko
([1]Nara Women's Univ.; [2]Kagoshima Univ.)

[submitted for publication]

Low-energy conformations of the S-peptide fragment (20 amino-acid residues long) of ribonuclease A were studied by Monte Carlo simulated annealing. The obtained lowest-energy structures have a-helices with different size and location, depending distinctively on the energy functions that allow for protonation and deprotonation of acidic amino-acid residues. The simulation started from completely random initial conformation and was performed without any bias towards a particular structure. The most conspicuous a-helices arose from the simulation when both Glu 9 and Asp 14 were assumed to be electrically neutral, whereas the resulting conformations became much less helical when Asp 14 rather than Glu 9 was allowed to have a negative charge. Together with experimental evidence that the a-helix in the S-peptide is most stable at pH 3.8, we consider the carboxyl group of Asp 14 should be protonated at this weakly acidic condition to facilitate the helix formation. In contrast, a negative charge at Asp 14 appears to function in support of a view that this residue is crucial to helix termination owing to its possibility to form a salt bridge with His 12. These results indicate that the conformation of the S-peptide depends considerably on the ionizing state of Asp 14.

I-E Development of Simulation Algorithms for Complex Systems

Developing a powerful simulation algorithm that can alleviate the multiple-minima problem is important in many complex systems. We have been advocating the uses of the so-called generalized-ensemble algorithms such as multicanonical algorithm and replica-exchange method.

I-E-1 Replica-Exchange Monte Carlo Methods for the Isobaric-Isothermal Ensemble

OKABE, Tsuneyasu[1]; KAWATA, Masaaki[2]; OKAMOTO, Yuko; MIKAMI, Masuhiro[3]
([1]JST; [2]Natl. Inst. Adv. Interdisc. Res.; [3]Natl. Inst. Mater. Chem. Res.)

[submitted for publication]

We propose an extension of Replica-Exchange Monte Carlo (REMC) method for canonical ensembles to isothermal-isobaric ensemble as an effective method to search for stable states quickly and widely in complex configuration space. We investigated the efficiency of the new method on a benchmark testing system which consists of 256 Lennard-Jones particles. The new method enables one to shorten dramatically the relaxation time of phase change from liquid structure to crystal structure in comparison with the conventional Monte Calro method.

I-E-2 Ab Initio Replica-Exchange Monte Carlo Method for Cluster Studies

ISHIKAWA, Yasuyuki[1]; SUGITA, Yuji; NISHIKAWA, Takeshi; OKAMOTO, Yuko
([1]Univ. Puerto Rico)

[*Chem. Phys. Lett.* **333**, 199 (2001)]

We have developed and implemented an algorithm for ab initio replica-exchange Monte Carlo simulations based on an ab initio correlated electronic structure theory. The many-body interactions in metal, semiconductor and molecular clusters are described by ab initio correlated method at the level of second-order Moller-Plesset perturbation theory. The replica-exchange Monte Carlo procedure allows for an efficient sampling of the global and low-lying local minima in a single simulation run, and thus, is ideally suited for locating energy minima of complex systems which possess a number of local minima. We have successfully applied the replica-exchange Monte Carlo method to the geometry optimization of the Li_6 cluster.

I-F Theory of Nonadiabatic Transition

I-F-1 Non-Adiabatic Transitions in a Two-State Exponential Potential Model

PICHL, Lukas[1]; OSHEROV, Vladimir I.[2]; NAKAMURA, Hiroki
([1]GUAS; [2]IMS and Inst. Chem. Phys., Russia)

[*J. Phys. A: Math. Gen.* **33**, 3361 (2000)]

A general two-state exponential potential model is investigated and the corresponding two-channel scattering problem is solved by means of semiclassical theory. The analytical expression for the non-adiabatic transition matrix yields a unified expression in the repulsive and previously studied attractive case. The final formulae are expressed in terms of model-independent quantities, *i.e.* the contour integrals of adiabatic local momenta. Oscillations of the overall transition probability below the crossing of diabatic potentials are observed in the case of strong coupling. The theory is demonstrated to work very well even at energies lower than the diabatic crossing region. Based on our results the unified theory of non-adiabatic transitions, covering the Landau-Zener-Stueckelberg and Rozen-Zener-Demkov models in such an energy range, is possible.

I-F-2 Complete Solutions of the Landau-Zener-Stueckelberg Curve Crossing Problems, and Their Generalizations and Applications

NAKAMURA, Hiroki

[*The Physics of Electronic and Atomic Collisions*, Y. Itikawa *et al.* Eds., Am. Inst. Phys., 495 (2000)]

The compact analytical complete solutions recently obtained for the two-state Landau-Zener-Stueckelberg problems are reviewed and explained. The theory covers both Landau-Zener (LZ) type in which the two diabatic potential curves cross with the same sign of slopes and the nonadiabatic tunneling (NT) type in which the potentials cross with different signs of slopes. The theory is applicable virtually in the whole range of energy and coupling strength and is convenient for practical use. The new theory for time-dependent nonadiabatic transition can be formulated from the time-independent theory of the LZ-type. The utilizability of the theory to various multi-channel problems and also to multi-dimesional problems is demonstrated and explained. The intriguing phenomenon of complete reflection which appears in the NT-case is explicitly utilized to propose a new type of molecular switching and to control molecular processes such as molecular photodissociation. Also proposed is a new way of controlling molecular processes by using time-dependent external fields. Finally, a trial to formulate a unified analytical theory to cover both Landau-Zener-Stueckelberg and Rosen-Zener-Demkov types of nonadiabatic transitions is briefly touched upon.

I-F-3 Complete Reflection in Two-State Crossing and Noncrossing Potential Systems

PICHL, Lukas[1]; NAKAMURA, Hiroki; HORACEK, Jiri[2]
([1]GUAS; [2]IMS and Charles Univ.)

[*J. Chem. Phys.* **113**, 906 (2000)]

A semiclassical study is made for the complete transmission and the complete reflection phenomena in two coupled molecular potential systems. The conditions for these phenomena to occur are expressed analytically in terms of nonadiabatic transition probabilities and phase integrals, which can be provided by the semiclassical theory. We also introduce an exactly solvable analytical model of diabatically avoided crossing, in which two diabatic potentials coupled by a constant coupling are close together in a certain spatial region. These models and phenomena may be useful in controlling various molecular processes in laser fields, since in the dressed or Floquet state formalism molecular potentials can be shifted up and down and are made to cross or avoid crossing with other potentials.

I-F-4 Nonadiabatic Transitions due to Curve Crossings: Complete Solutions of the Landau-Zener-Stueckelberg Problems and Their Applications

ZHU, Chaoyuan; TERANISHI, Yoshiaki[1]; NAKAMURA, Hiroki
([1]IMS and Inst. Phys. Chem. Res.)

[*Adv. Chem. Phys.* in press]

I. Introduction
II. Physical Significance of Level Crossing
III. Complete Solutions of the Two-State Landau-Zener-Stueckdberg Problems
    A. Brief Historical Survey
    B. Complete Solutions
        (1) Landau-Zener Case
        (2) Nonadiabatic Tunneling Case
IV. How to Deal with Multi-Channel and Multi-Dimensional Problems
    A. Multi-Channel Processes
        (1) General Framework
        (2) Numerical Applications
    B. Multi-Dimensional Problems
V. Other Models
    A. Exponential Potential Model
    B. Rosen-Zencr-Demkov Model
    C. Special Cases of Exponential Potential Model
    D. Remarks
VI. Time-Dependent Level Crossings
    A. Complete Solutions of the Quadratic Model
    B. Generalizations and Applications
    C. Other Models
VII. New Way of Controlling Molecular Processes by Time-Dependent External Fields

- A. Basic Theory
- B. Control by Laser Field
  - (1) Landau-Zener Type of Nonadiabatic Transition
  - (2) Rosen-Zener Type of Nonadiabatic Transition
  - (3) Exponential Type of Nonadiabatic Transition

VIII. Future Perspectives

I-F-5 New Type of Nonadiabatic Dynamics: Transitions between Asymptotically Degenerate States

OSHEROV, Vladimir I.[1]; NAKAMURA, Hiroki
([1]IMS and Inst. Chem. Phys., Russia)

Nonadiabatic transitions between asymptotically degenerate potential curves are discussed. Both crossing and non-crossing two-coupled-Morse-potential systems are studied semiclassically as well as quantum mechanically. Conditions for the appearance of the new type of nonadiabatic transition are clarified. The case of inverse power potentials at infinity is also analyzed. New expressions of nonadiabatic transition probability are obtained.

I-G Theoretical Studies of Chemical Reaction Dynamics

I-G-1 Electronically Adiabatic Chemical Reactions Analyzed by the Semiclassical Theory of Nonadiabatic Transition

ZHU, Chaoyuan; NAKAMURA, Hiroki; NOBUSADA, Katsuyuki[1]
([1]Hokkaido Univ.)

[*Phys. Chem. Phys.* **2**, 557 (2000)]

The previously proposed qualitative conceptualization of heavy-light-heavy (HLH) chemical reactions on a single potential energy surface (PES) as vibrationally nonadiabatic transitions at avoided crossings along the potential ridge lines is confirmed and further extended. An analytical as well as quantitative analysis of three-dimensional HLH reactions is carried out by applying the new semiclassical theory of nonadiabatic transition established by Zhu and Nakamura. About one thousand avoided crossings which appear in the sea of adiabatic potential curves obtained in the hyperspherical coordinate approach are classified into relevant and irrelevant ones for reactive transitions by introducing a certain diabatic decoupling procedure based on the dimensionless parameter of the new semiclassical theory. Thus about one hundred of three kinds of avoided crossings relevant for reactive transitions are specified and treated analytically. The cumulative reaction probabilities can be quite nicely reproduced quantitatively. This indicates that the clarification and conceptualization of reaction mechanisms can be done even analytically. State-to-state reaction processes can be qualitatively nicely comprehended as before, but cannot be quantitatively well reproduced, simply because inelastic transitions are not necessarily localized and cannot be well comprehended in terms of nonadiabatic transitions due to avoided crossings. An interesting series of avoided crossings responsible for rotationally inelastic transitions are found at energy lower than the threshold of reaction in the case of exo- or endoergic reaction.

I-G-2 Quantum Reaction Dynamics of O(^{3}P) + HCl on a New Ab Initio Potential Energy Surface

NOBUSADA, Katsuyuki[1]; NAKAMURA, Hiroki; LIN, Yongjing[2]; RAMACHANDRAN, B.[2]
([1]Hokkaido Univ.; [2]Louisiana Tech. Univ.)

[*J. Chem. Phys.* **113**, 1018 (2000)]

Quantum reaction dynamics of O(^{3}P) + HCl ↔ OH + Cl is studied by using a new *ab initio* potential energy surface calculated by Ramachandran et al. [*J. Chem. Phys.* **111**, 3862 (1999)]. The hyperspherical *elliptic* coordinate approach is applied with an emphasis on elucidating reaction dynamics for J (total angular momentum quantum number) = 0. In terms of the previously established concept that reactive transitions are nothing but vibrationally nonadiabatic transitions at important avoided crossings, clear interpretations are given for the following dynamical features: (i) reactivity depending on potential energy surface topography, (ii) final rotational state distributions for specified initial rovibrational states, and (iii) resonance structures appearing in some reactions. Thermal rate constants are approximately estimated from the present $J = 0$ results by using the *J-shift* approximation. The present results are compared with our previous ones based on the different potential energy surface calculated by Koizumi-Schatz-Cordon (KSG). The calculated adiabatic potential energy curves of the present new surface have deep wells in the OH + Cl channel in contrast to the KSG potential energy surface. Consequently, the new surface leads to quite different dynamics from those on the KSG surface. Comparisons with the results obtained by quasiclassical trajectory calculations are also made.

I-G-3 Quantum-Classical Correspondence in the O(^{3}P) + HCl and Cl(^{2}P) + OH Reactions for Total Angular Momentum $J = 0$

LIN, Yongjing[1]; RAMACHANDRAN, B.[1]; NOBUSADA, Katsuyuki[2]; NAKAMURA, Hiroki
([1]Lousiana Tech. Univ.; [2]Hokkaido Univ.)

A method for carrying out quasiclassical trajectory (QCT) calculations of A + BC (v,j) reactive collisions for the special case of the total angular momentum $J = 0$

is described. Since quantum reactive scattering calculations involving heavier atoms are not straightforward for the $J > 0$ case, this method is useful to establish the extent to which classical mechanics is applicable to a particular reaction. The method is tested by comparing the results of trajectory calculations for the $J = 0$ case with analogous quantum mechanical (QM) calculations for the O(^{3}P) + HCl reaction and the reverse reaction Cl(^{2}P) + OH. The S4 potential surface, which is based on MRCI+Q/cc-pVTZ energies scaled by the Scaled External Correlation method [B. Ramachandran, E. A. Schrader III, J. Senekowitsch and R. E. Wyatt, *J. Chem. Phys.* **111**, 3862 (1999)], is used for these calculations. The QCT and QM cumulative reaction probabilities are found to be in good agreement, especially for the Cl + OH reaction. The agreement between the two types of state-resolved reaction probabilities is less striking but improves considerably as the initial diatomic rotational quantum number j increases. A comparison is also made between the exact and J-shifted QCT thermal rate coefficients. These are found to be in excellent agreement, which is in keeping with similar agreement observed in the case of the quantum mechanical exact and J-shifted thermal rate coefficients.

I-G-4 New Implementation of the Trajectory Surface Hopping Method with Use of the Zhu-Nakamura Theory

ZHU, Chaoyuan; NAKAMURA, Hiroki; NOBUSADA, Katsuyuki[1]
([1]Hokkaido Univ.)

The Zhu-Nakamura theory, the complete set of analytical solutions of the Landau-Zener-Stueckelberg curve crossing problems, can be applied to multi-dimensional reaction dynamics involving electronically nonadiabatic transitions due to potential energy surface crossings. The theory can be incorporated into various types of semiclassical propagation methods such as the trajectory surface hopping method, the semiclassical method with use of the initial value representation and the cellular frozen Gaussian propagation method. Even the phases due to nonadiabatic transition are provided by the Zhu-Nakamura theory and can be taken into account. The simplest application of the theory is the usage of nonadiabatic transition probability in the trajectory surface hopping method. Even the classically forbidden transitions can be properly treated. First application is made to the collinear H_3^+ reaction system and shows very encouraging good agreement with the quantum mechanical results.

I-G-5 Diabatic Slow Variable Discretization Approach in Time-Independent Reactive Scattering Calculations

MIL'NIKOV, Gennady V.[1]; NAKAMURA, Hiroki
([1]IMS and Inst. Struct. macrokinetics, Russia)

We propose a new recipe for the R matrix propagation which combines advantages of the slow Variable Discretization (SVD) and the diabatic-by-sector approach. Within the framework of the hyperspherical coordinate approach this novel scheme allows us to avoid calculations of surface functions for most of the DVR (discrete variable representation) radial points, which significantly reduces the computational time and required memory with the simplicity and the accuracy of the SVD preserved. The properties of the R-matrix propagation as a variational procedure are discussed to justify a proper choice of numerical parameters. This is checked by a test calculation of the reaction O(^{3}P) + HCl → OH + Cl using a LEPS potential energy surface (PES). The applicability of the method is further demonstrated by accurate quantum calculations of the endoergic reaction $H(^2S) + O_2(^3\Sigma_g^-) \rightarrow OH(^2\Pi) + O(^3P)$.

I-G-6 Quantum Dynamics in the DH_2^+ Reaction System

KAMISAKA, Hideyuki[1]; NAKAMURA, Hiroki; NOBUSADA, Katsuyuki[2]
([1]GUAS; [2]Hokkaido Univ.)

As one of the typical electronically nonadiabatic chemical reactions, we have carried out quantum mechanically accurate calculations of the title system. The potential energy surface used is an analytical fit of the new ab initio calculations done by Ichihara *et al*. For the quantum dynamics the hyperspherical elliptic coordinate system is employed. At low energies where only the electronically adiabatic processes occur, the overall feature can be explained by the statistics basically because of the deep potential well in the ground electronic potential surface. There appears, however, an interesting deviation from the statistics in the case of electronically nonadiabatic reactions.

I-H New Way of Controlling Molelular Processes

I-H-1 Laser Control of Molecular Photodissociation with Use of the Complete Reflection Phenomenon

NAGAYA, Kuninobu[1]; TERANISHI, Yoshiaki[2]; NAKAMURA, Hiroki
([1]GUAS; [2]Inst. Phys. Chem. Res.)

[*J. Chem. Phys.* in press]

A new idea of controlling molecular photodissociation branching by a stationary laser field is proposed by utilizing the unusual intriguing quantum mechanical phenomenon of complete reflection. By introducing the Floquet (or dressed) state formalism, we can artificially create potential curve crossings, which can be used to control molecular processes. Our control scheme presented here is summarized as follows. First, we prepare an appropriate vibrationally excited state in the ground electronic state, and at the same time by applying a stationary laser field of the frequency ω we create two nonadiabatic tunneling (NT) type curve crossings between the ground electronic bound state shifted up by one photon energy $\hbar\omega$ and the excited electronic state with two dissociative channels. In the NT-type of curve crossing where the two diabatic potential curves cross with opposite signs of slopes, it is known that the complete reflection phenomenon occurs at certain discrete energies. By adjusting the laser frequency to satisfy the complete reflection condition at the NT type curve crossing in one channel, the complete dissociation into the other channel can be realized. By taking one-and two-dimensional models which mimic the HOD molecule and using a wave packet propagation method, it is numerically demonstrated that a molecule can be dissociated into any desired channel selectively. Selective dissociation can be realized even into such a channel that cannot be achieved in the ordinary photodissociation because of a potential barrier in the excited electronic state.

I-H-2 New Way of Controlling Molecular Processes by Lasers

TERANISHI, Yoshiaki[1]; NAGAYA, Kuninobu[2]; NAKAMURA, Hiroki
([1]Inst. Phys. Chem. Res.; [2]GUAS)

[*Quantum Control of Molecular Reaction Dynamics*, R. J. Gordon and Y. Fujimura Ed., World Scientific, in press]

Control of molecular processes by lasers has attracted much attention recently, and several schemes have been proposed such as coherent control, pump-dump method, pulse-shape driven method, adiabatic rapid passage with linear chirp, and π-pulse. Considering the importance of nonadiabatic transitions due to curve crossing not only in ordinary molecular processes but also in molecular processes induced by lasers, we have proposed a new way of controlling nonadiabatic transitions by sweeping laser frequency and/or intensity at curve crossings among the dressed (or Floquet) states. By using the newly developed time-dependent theory of nonadiabatic transitions, we can analytically formulate appropriate control conditions. On the other hand, the intriguing phenomenon of complete reflection in the nonadiabatic tunneling (NT) type transition in the time-independent framework has been utilized to propose a new mechanism of molecular switching and a new possibility of controlling molecular photodissociation. These new ideas are briefly reviewed in this report.

I-I New Methods to Treat Scattering Problems

I-I-1 Analytical Treatment of Singular Equations in Dissociative Recombination

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([1]GUAS; [2]Charles Univ.)

[*Comput. Phys. Commun.* **124**, 1 (2000)]

The Lippmann-Schwinger type singular integral equation, which arises in the multi-channel quantum defect theory of dissociative recombination process, is investigated. The singularity of its kernel is treated analytically by introducing an energy dependent quadrature. In many cases of physical interest the energy-dependent coupling potential, which gives the integral kernel of the equation, is quasi-separable in a way that allows to write down an analytical solution. The analytical treatment as well as the new solution are illustrated by taking the H_2^+ as an example. Our method is demonstrated to be much better than the conventional ones, such as the first order perturbation theory and the grid method.

I-I-2 Stable and Efficient Evaluation of Green's Function in Scattering Problem

MIL'NIKOV, Gennady V.[1]; NAKAMURA, Hiroki; HORACEK, Jiri[2]
([1]IMS and Inst. Struct. macrokinetics, Russia; [2]IMS and Charles Univ.)

A new methodology similar to the R-matrix propagation technique is invoked to propose the practical recipe for efficiently calculating the Green's function in scattering problem. High accuracy of the proposed approach is demonstrated by taking examples of very deep tunneling and complex-valued nonlocal potential which describes low-energy dissociative attachment process between electron and molecules.

I-J Theoretical Study of Multi-Dimensional Tunneling

I-J-1 Theoretical Study of Multidimensional Proton Tunneling in the Excited State of Tropolone

WOJCIK, Marek J.[1]; NAKAMURA, Hiroki; IWATA, Suehiro; TATARA, Wiktor[1]
([1]Jagiellonian Univ.)

[*J. Chem. Phys.* **112**, 6322 (2000)]

Ab initio CIS/6-3lG** and CIS/6-3l ++G** calculations have been carried out in the Ã-state of tropolone for the stable and saddle point structures. The calculated energies and geometries have been compared with the previous results of Vener *et al.* The energy barrier for the proton tunneling amounts to 12.0 kcal/mol from the CIS/6-31G** calculations, and l3.0 kcal/mol from the CIS/6-31++G** calculations. The normal mode frequencies have been computed including modes coupled to the proton tunneling mode. Two-dimensional and three-dimensional model potentials, formed from symmetric mode coupling potential and squeezed double well potential, have been fitted to the calculated energy barrier, geometries, and frequencies, and used to analyze proton dynamics. The calculated energy splittings for different vibrationally excited states have been compared with the available experimental data. The CIS/6-3l ++G** calculation gives good estimation of the tunneling energy splitting in the vibrationally ground state of tropolone. The model PES explain monotonic decrease in tunneling splittings with the excitation of the out-of-plane modes, however underestimate the actual splittings. The increase of the tunneling splitting with the excitation of the v_{13} and v_{14} modes is qualitatively correct.

I-K Theoretical Studies of Ultrafast Nonlinear Optical Spectroscopy of Molecules in Condensed Phases

Nonlinear optical interactions of laser fields with matter provide powerful spectroscopic tools for the understanding of microscopic interactions and dynamics processes. We attempt to provide theoretical basis for a wide class of nonlinear spectroscopic techniques, focusing on the underlying physical processes in the condensed phases.

I-K-1 Two-Dimensional Line Shape Analysis of Photon Echo Signal

OKUMURA, Ko; TOKMAKOFF, Andrei[1]; TANIMURA, Yoshitaka
([1]MIT)

[*Chem. Phys. Lett.* **314**, 488(1999)]

We analyze the two-dimensional (2D) line shape obtained by 2D Fourier transforming the time-domain response of a photon echo signal as a function of the two coherence periods, t_1 and t_3. The line shape obtained for a two level system with homogeneous and inhomogeneous broadening is shown to be sensitive to the magnitude of both of these line-broadening mechanisms. It is shown that the ellipticity of the 2D line shape can be related to the ratio of homogeneous to inhomogeneous broadening.

I-K-2 Cage Dynamics in the Third-Order Off-Resonant Response of Liquid Molecules: A Theoretical Realization

OKUMURA, Ko; BAGCHI, Biman[1]; TANIMURA, Yoshitaka
([1]Indian Inst. Sci.)

[*Bull. Chem. Soc. Jpn.* **73**, 873 (2000)]

It is generally believed that the ultrafast initial spectroscopic response from the molecules in the condensed phase originates from small amplitude inertial motions within the cage formed by the nearest-neighbor solvent molecules surrounding the probe, or the cage effect. However, no quantitative estimate of this dynamics has been available for the currently popular experiments which measure the third-order off-resonant response. In this work, we fill this gap by a microscopic approach and demonstrate that the cage dynamics alone can produce the initial rise in the subpicosecond (200[fs]) range in the third-order response. A simple analytical expression for the initial Gaussian time constant relevant to various kinds of the third-order off-resonant experiments is presented, which is found to be rather strongly dependent on the temperature. Connection with the non-polar solvation dynamics is also discussed.

I-K-3 Two-Dimensional Spectroscopy for Harmonic Vibrational Modes with Nonlinear System-Bath Interactions: Gaussian-Markovian Case

TANIMURA, Yoshitaka; STEFFEN, Thomas[1]
([1]Univ. Groningen)

[*J. Phys. Soc. Jpn.* **69**, 4095 (2000)]

The relaxation processes in a quantum system nonlinearly coupled to a harmonic Gaussian-Markovian heat bath are investigated by the quantum Fokker-Planck equation in the hierarchy form. This model describes frequency fluctuations in the quantum system with an arbitrary correlation time and thus bridges the gap between the Brownian oscillator model and the stochastic model by Anderson and Kubo. The effects of the finite correlation time and the system-bath coupling strength are studied for a harmonic model system by numerically integrating the equation of motion. The one-time correlation function of the system coordinate, which is measured in conventional Raman and infrared absorption experiments, already reflects the inhomogeneous character of the relaxation process. The finite correlation time of the frequency fluctuations, however, is directly evident only in the two- and three-time correlation function as probed by multidimensional spectroscopic techniques such as the Raman echo and the fifth-order 2D Raman experiment.

I-K-4 Two-Dimensional Spectroscopy and the Harmonically Coupled Anharmonic Oscillators

OKUMURA, Ko; JONAS, M. David[1]; TANIMURA, Yoshitaka
([1]Univ. Colorado)

Experimentally it is established that the 4th-order anharmonicity plays significant roles in many molecules; based on the local (anharmonic) modes picture with couplings between them, the Darling-Dennison coupling manifests itself, which has been confirmed experimentally. It has been shown that this order of anharmonicity can be selectively studied via the 7th order off-resonant optical processes (Okumura and Tanimura, *J. Chem. Phys.* **106**, 1687 (1997)). We obtained fairly compact analytical result for the 7th-order signal and numerically present the signal from CH stretch vibrations in methylene chloride as two dimensional contour maps. By virtue of the two-dimensionality the results demonstrate the possibility of giving further insight into such mechanism that is not available in the one-dimensional high resolution spectroscopy.

I-K-5 Two-Dimensional Raman and Infrared Signals Measured from Different Phase-Matching Conditions

KATO, Tsuyoshi; TANIMURA, Yoshitaka

We developed a theoretical method that can explicitly treat the phase-matching condition of two-dimensional optical measurements. This method might be a rational tool for the analysis of observed signals under non-impulsive excitation. We use this method to separate the contribution of the signal from different Liouville pathways associated with the different phase-matched condition. It is expected that the effects of mode coupling, anharmonicity of the system potential and nonlinearity of the polarizability will be pronounced by the spatial discrimination of the signal, which can be achived experimentally.

I-L Quantum dynamics in the condensed phases

We investigate quantum dynamics of molecules in the condensed phases by means of various statistical physics approaches involving the path integral and Fokker-Planck equation approaches for a reduced density matrix. Effects of dissipation on a quantum rotator, proton tunneling and electron transfer processes are investigated and compared with the classical dynamics.

I-L-1 Path-Integral Approach to Rotational Relaxation Processes of a Molecule in Solvation

SUZUKI, Yoko; TANIMURA, Yoshitaka

A two-dimensional rotator coupled to a Brownian oscillators bath is considered to study rotational relaxation processes in a dissipative environment. Nonequilibrium generating functional of the rotator is evaluated by transforming the Hamiltonian in diagonal form and by carrying out the functional integrals of the bath coordinates and the rotator angel. The difference between the free particle and the rotator arises from the cyclic boundary condition supplied for the rotator angel. Using the generating functional, we obtain the analytical expression of optical response function, which is defined by the two-time correlation function of dipole moment or polarizability of the rotator, is obtained from the generating functional. The qunatal dynamics of rotator under the influence of the heat-bath is investigated by calculating Raman spectrum for various temperatures and the coupling strength between the rotator and the bath.

I-L-2 Proton Tunneling in a Dissipative Environment: Raman Response and Reaction Rate

TANIMURA, Yoshitaka

A double well potential system coupled to a colored Brownian oscillators bath is considered to study tunneling dynamics in a dissipative environment. The quantum Fokker-Planck equation for a colored nose bath in a low temperature is reduced in a multi-dimensional hierarchy form. A chemical reaction rate and Raman response spectrum are calculated for various coupling strength and temperature. Compared with the classical results, which are obtained by solving classical Fokker-Planck equation, we investigate the effects of tunneling processes on the reaction rate and spectrum. In the quantal case, the low frequency peak is observed in the Raman spectrum, which is due to the level splitting of vibrational levels induced by tunneling.

I-M Soft Matter Physics in Biomimetic Systems

Various efforts have been undertaken to make smart things useful in daily life by mimicking biomaterials. Such field has been propelled mainly from technological and practical viewpoint. However, this field has a great potential to give new ideas, concepts, and problems to soft matter physics as pure science. We have been studied two such examples, *i.e.*, nacre, which typically constitutes seashells, and a certain kind of artificial muscle, which can be driven by a small electric field.

I-M-1 On the Toughness of Biocomposites

DE GENNES, Pierre-Gilles[1]; OKUMURA, Ko
([1]Collège de France)

[*C. R. Acad. Sci. Paris* **IV**, 257 (2000)]

The fracture energy G of nacre (a stacking of aragonite/organic layers) is much larger than the corresponding energy G_0 for pure aragonite (although the organic cement thickness d_0 is very small: nanometers). We present here a qualitative explanation for this difference. The basic idea is that a weak cement reduces drastically the stress concentration near the fracture tip.

I-M-2 Why is Nacre Strong?: Elastic Theory and Fracture Mechanics for Biocomposites with Stratified Structures

OKUMURA, Ko; DE GENNES, Pierre-Gilles[1]
([1]Collège de France)

[*Eur. Phys. J. E.* submitted]

Nacre, stratified ceramic layers surrounded by organic matrix, is a tough material found inside certain seashells. We construct a coarse grained elastic energy for such an anisotropic system and present an analytic solution for a notch crack normal to the stratified sheets. This analysis proves the reduction in stress concentration which was announced in our earlier work (P. G. de Gennes and K. Okumura, *C. R. Acad. Sci. Paris* t.1, Serie IV, 257 (2000)) and the related increase in toughness.

I-M-3 Mechanoelectric Effects in Ionic Gels

DE GENNES, Pierre-Gilles[1]; OKUMURA, Ko; SHAHINPOOR, Mohsen[2]; KIM, Kwang J.[2]
([1]Collège de France; [2]Univ. New Mexico Albuquerque, U. S. A.)

[*Europhys. Lett.* **50**, 513 (2000)]

Certain fluorinated ion-exchange membranes, when swollen and suitably plated by conducting electrodes, display a spontaneous curvature increasing with the applied electric field E. There is also an inverse effect, where an imposed curvature induces an electric field (in open circuit conditions). We present here a compact description of these effects in the linear regime, and in static conditions: this is based on linear irreversible thermodynamics, with two driving forces (E and a water pressure gradient Δp) and two fluxes (electric current and water current). We also give some qualitative estimates of the three Onsager coefficients, which come into play.

I-N Liquid-Liquid Phase Transition of Water and Its Potential Surface

Water in supercooled state exhibits many anomalous properties such as divergence of the thermodynamic response functions, liquid-liquid (amorphous-amorphous) transition. Recent computer simulation and theoretical model predict this kind of transition. In view of experimental aspect, it is hard to follow this transition since the area that the transition is expected to be observed in temperature-pressure diagram is inaccessible by experiment, called 'no man's land.' Careful examination of the supercooled water show various kind of unique properties, in particular in configuration space.

I-N-1 The Melting Temperature of Proton-Disordered Hexagonal Ice: A Computer Simulation of TIP4P Model of Water

GAO, Guangtu[1]; ZENG, Xiao C.[1]; TANAKA, Hideki
([1]Univ. Nebraska)

[*J. Chem. Phys.* **112**, 8534 (2000).]

We report computer simulation results of free energies of proton-disordered hexagonal ice and liquid water at atmospheric pressure with TIP4P model of water. A new reference system is used to calculate the free energy of the ice phase. The melting point of proton-disordered hexagonal ice at atmospheric pressure is found to be T_m = 238 K. This result is consistent with a previous estimation, 230 K < T_m < 250 K, from molecular dynamic simulation of the surface melting of the proton-disordered hexagonal ice [G.-J. Kroes, *Surf. Sci.* **275**, 365 (1992)].

I-N-2 Hydrogen Bonds between Water Molecules: Thermal Expansivity of Ice and Water

TANAKA, Hideki

[*Phys. Chem. Chem. Phys.* **2**, 1595 (2000)]

The free energy components of two low pressure crystalline ices and an amorphous form of water are calculated over a wide range of temperatures. The Gibbs free energy at a given temperature is minimized with respect to volume of a system. This enables us to evaluate a thermal expansivity at fixed temperature and pressure from only intermolecular interaction potential. The negative thermal expansivity in low temperature is obtained for both crystalline ices and an amorphous form, which arises from the bending motion of hydrogen bonded molecules.

I-N-3 Potential Energy Surfaces of Supercooled Water: Intrabasin and Interbasin Structures Explored by Quenching, Normal Mode Excitation, and Basin Hopping

TANAKA, Hideki

[*J. Chem. Phys.* **113**, 11202 (2000)]

We investigate the potential energy surfaces of supercooled water; both intrabasin structures and distributions of the potential energy basins in configuration space by the steepest descent quenching and the normal mode excitation. The paths from liquid configurations to the corresponding local energy minima and the root mean square distance exhibit different characters below and above the temperature 213 K where the thermodynamics and structural properties change abruptly. The root mean square distance in the temperature range (298 K to 173 K) is larger than the corresponding harmonic oscillator system and it drastically increases above 223 K. Also increases the complexity along the steepest descent path by increasing the number of inflection points. In order to investigate the other potential energy basins distributed in the vicinity of the (central) basin that the molecular dynamics trajectory visits, the distributions of these basins are examined by the normal mode excitation. The number of distinct basins increases with increasing temperature in the same volume of configuration space. The minimum potential energy of the adjacent basin at low temperature is almost always higher than the minimum potential energy of the central basin while that of the adjacent basin at high temperature is comparable to the central basin. The locations of the other basin centers are mostly orthogonal to the normal mode excitation. The potential energy surfaces are also examined by the basin hopping technique to seek for lower energy configurations started with a random and high-energy molecular arrangement. It is found that energetically more stable molecules aggregate rather heterogeneously in the intermediate energy levels which are hardly observed in the simulation while the stable molecules distribute homogeneously in the lowest energy levels.

I-N-4 Molecular Dynamics Study of the Connectivity of Water Molecules in Supercooled States

TANAKA, Hideki

[*Mol. Liq.* in press]

We examine distributions of four-coordinated supercooled water molecules in two state points where the densities are considerably different from each other. It is found, although the coordination numbers are all four in local energy minimum structures free from thermal excitation, the magnitude of the connectivity of tetrahedrally coordinated molecules differs significantly between two supercooled states. We also investigate thermodynamic properties for liquids composed of two kinds of deformed water molecules having wider bond angles in order to compare the properties of those liquids with those of a realistic water model.

I-N-5 Ice Nanotube: What Does the Unit Cell Look Like?

KOGA, Kenichiro[1]; PARRA, R. D.[2]; TANAKA, Hideki; ZENG, Xiao C.[2]
([1]Fukuoka Univ. Edu.; [2]Univ. Nebraska)

[*J. Chem. Phys.* **113**, 5037 (2000)]

It is discovered that for an n-gonal ice nanotube built from stacking a single n-gonal ring of water, the unit cell consists of two stacked n-gonal rings. In one ring the O-H arms of water molecules line up clockwise whereas in the other ring the O-H arms line up counterclockwise. Among the n-gonal ice nanotubes examined, the pentagonal or hexagonal ice nanotube appears to be the most stable.

I-N-6 First-Order Transition in Confined Water between High Density Liquid and Low Density Amorphous Phases

KOGA, Kenichiro[1]; TANAKA, Hideki; ZENG, Xiao C.[2]
([1]Fukuoka Univ. Edu.; [2]Univ. Nebraska)

[*Nature* **406**, 564 (2000)]

Department of Chemistry and Center for Materials Analysis, University of Nebraska, Lincoln, Nebraska 68588, USA Supercooled water and amorphous ice continuously intrigue us withtheir rich metastable phase behaviour. In eighties, a high density amorphous to low density amorphous (HDA-LDA) solid-to-solid phase transition below 140 K was uncovered by Mishima and coworkers. In mid-nineties, a high density liquid to low density liquid (HDL-LDL) liquid-to-liquid phase transition was reported from computer simulations of supercooled water. Recently, a fragile-to-strong liquid transition was also proposed in supercooled water near 228 K, and was observed experimentally in supercooled bilayer water confined in-between hydrophilic slit pores. Here, we report molecular dynamics evidence suggesting a new type of first-order phase transition above the freezing temperature of bulk ice Ih at 0.1 MPa—a liquid-to-bilayer amorphous transition. This metastable phase transition appears uniquely when a two-layer water is confined in a hydrophobic slit pore at a width of less than one nanometer, that is, in a quasi-two-dimensional water. Some characteristics of this first-order transition resemble those found in tetrahedral substances such as liquid silicon, liquid carbon and liquid phosphorus.

I-O Development of Techniques for Prediction of Conformations and Applications to Proteins and Organic Compounds

Various techniques of Prediction of Conformations have been developed in this decades including proteins and organic compounds. However, a prediction of protein 3D strcutures is still unsolved and difficult problem in the area of molecular biophysics. Therefore, the elucidation of the basic mechanism of protein folding is significant to develop a prediction method of protein 3D strcuture. Currently, we are treating simple spin model of the behabior of a protein and trying to understand the basic physics of protein folding. On the other hand, development of a modeling technique of organic compounds in terms of the interactions with a protein is also important especially in the field of drug design. We have developed a new method of QSAR (quantitative structure activity relationship) analysis which can be applied to modeling of drugs. Furthermore, we have applied our modeling techniques to the actual protein, human serum transferrin, and a organic photobase compounds.

I-O-1 Kinetics of a Finite One-Dimensional Spin System as a Model for Protein Folding

KIKUCHI, Takeshi
(IMS and Kurashiki Univ. Sci. Arts)

[*Biophys. Chem.* **85**, 93 (2000)]

Simple spin models were used to analyze the kinetic nature of lowest energy state formation of the spin systems as models of protein folding kinetics in the this work. The models employed in this work were based on the spin systems as models of biopolymers previously proposed for the analysis of the equilibrium nature of transition.[1)] In particular, the effect of frustrations on the kinetics was investigated with the Monte Calro simulations. The results showed that the kinetics of the present systems are characterized by the ratio of foldables (pathways on the energy landscape that leads to the lowest energy state) and the temperature dependence of the mean first passage time of fodables. These properties of the present spin model are corresponding to kinetic behavior of actural proteins. The important thing of the kinetics ofa zero frustration system is the passage from the Levinthal phase at higher temperature to the Arrhenius phase at lower temperature.

Reference

1) T. Kikuchi, *Biophys. Chem.* **65**, 109 (1997).

I-O-2 Molecular Modeling of Human Serum Transferrin for Rationalizing the Changes in Its Physicochemical Properties Induced by Iron Binding. Implication of the Mechanism of Binding to Its Receptor

YAJIMA, Hirofumi[1]; SAKAJIRI, Tetsuya[1]; KIKUCHI, Takeshi[2]; ISHII, Tadahiro[1]
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[*J. Protein Chem.* **19**, 215 (2000)]

In order to rationalize the resulting physicochemical properties of human serum-transferrin (Stf) and the Stf-receptor (TfR) recognition process, we have tried to predict the 3D structures of apo- and iron-loaded Stf using a homology modeling technique to study the changes in the structural characteristics that would take place upon the uptake of iron by Stf in solution. Therein, the crystal structures of both forms for ovotransferrin were used as templates for the Stf modeling. The modeled structure of Stf brought about a satisfactory interpretation for the tyoical physico-chemical properties such that (1) Stf has a negative electrophoretic mobility and its value increases with iron uptake, and (2) the radius of gyration (Rg) of Tf decreases with iron uptake. Moreover, in view of the findings from our capillary electrophoresis experiments, it is inferred that the connecting (bridge) and its neighboring region associated with a surface exposure of negative charge plays an important role in the Stf-receptor recognition process.

I-O-3 A CoMFA Analysis with Conformational Propensity: An Attempt to Analyze the SAR of a Set of Moleculas with Different Conformational Flexibility Using a 3D-QSAR Method

GOHDA, Keigo[1]; MORI, Ichiro[2]; OHTA, Daisaku[3]; KIKUCHI, Takeshi[4]
([1]Novartis Pharma; [2]GlaxoWelcome; [3]Osaka Pref. Univ; [4]IMS and Kurashiki Univ. Sci. Arts)

[*J. Comput. Aided Mol. Des.* **14**, 265 (2000)]

CoMFA analysis, a widely used 3D-QSAR method, has limitations to handle a set of SAR data containing diverse conformarional flexibility since it does not explicitly include the conforamtional entropic effects into the analysis. We presented in thi work an attempt to incorporate the confromational entropy effects of a molecule into a 3D-QSAR analysis. Our attempt is based on the assumption that the conformational entropic loss of a ligand upon making a ligand-receptor complex is small if the ligand in an unbound state has a conformational propensity to adopt an active conformation in a complex state. The conformational propensity is defined as the population ratio of active conformations to stable conformations. The active conformation is defined from the structure of a compound with a rigid structure with high activity. We applied the present method to 20 imidazoleglycerol phosphatase inhibitors with various conformational flexibility. The results show that our method improved the predictability compared with the stadard CoMFA method.

I-O-4 Study on Photobase Generation from α-Aminoketones: Photocrosslinking of Epoxides with Carboxlic Acids

KURA, Hideaki[1]; OKA, Hidetaka[1]; BIRBAUM, Jean-Luvc[1]; KIKUCHI, Takeshi[2]
([1]Ciba Specialty Chem.; [2]IMS and Kurashiki Univ. Sci. Arts)

[*J. Photopolym. Sci. Technol.* **13**, 145 (2000)]

It was demonstrated that α-Aminoketones work effectively as photobase generators in epoxy-based compositions in this work. After irradiation they accelerate the thermal crosslinking reaction of phenol novolac epoxy resin with polyacrylate having carboxylic acid groups despite of their high latency before irradiated. The accelaration effect depends on the structure of the photogenerated amines. Conformational population of the α-aminoketones and the related compounds was also calculated based on the molecular mechanics. The results suggest that folded conformations contribute to the latency of the amine moiety. In the conformations, the bulky benzoyl group of the aminoketone sheilds the amino nitrogen from acidic species present in the composition. By irradiation, the benzoyl part is cleaved and the active tertiary amine base with small substituents is eventually liberated. The investigation using model amines supported the explanation. The compositions used for this study can be utilized in the base-catalyzed imaging application.

I-P Microscopic Solvation of Alkali Atom and Aggregates in Polar Solvent Clusters

The understanding of the structure and dynamics of solvated electron is of fundamental importance in the wide areas of chemistry, physics and biology. Clusters containing polar solvent molecules and a single alkali atom and/or aggregates can be regarded as a prototype for studying this intriguing subject. They are expected to give size dependent information on the spontaneous ionization of the alkali metal and the formation of the solvated electron. To elucidate the electronic nature of the clusters at the molecular level, we have carried out ab initio study in collaboration with the spectroscopic experiments.

I-P-1 Solvation Process of Na_m in Small Ammonia Clusters: Photoelectron Spectroscopy of $Na_m^-(NH_3)_n$ ($m \leq 3$)

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[*J. Electron. Spectrosc. Relat. Phenom.* **106**, 127 (2000)]

Photoelectron spectra (PESs) of $Na_m^-(NH_3)_n$ ($m \leq 3$) are investigated to explore the solvation of sodium atom and its aggregates in small ammonia clusters. For $Na^-(NH_3)_n$, we examine the PESs with an improved resolution and confirm the spontaneous ionization of Na atom in small clusters. As for $Na_2^-(NH_3)_n$ ($n \leq 8$), vertical detachment energy (VDE) of the transition from the anion to the neutral ground state is found to shift to the red with respect to that of $Na_2(X^1\Sigma_g^+)$, while that of the first excited state derived from $Na_2(a^3\Sigma_u^+)$ increases gradually for $n \geq 4$. In addition, the transitions to the higher-excited states derived from those correlated to the $3^2S + 3^2P$ asymptote are found to be shifted rapidly to the red and become almost degenerate with the $a^3\Sigma_u^+$–type transition. The extensive spectral change is ascribed to the asymmetrical ammoniation and spontaneous ionization of Na_2 in small clusters. We also find the drastic change in the PESs of $Na_3^-(NH_3)_n$; the neutral ground ($^2\Sigma_u^+$–type) and first excited ($^2\Sigma_g^+$–type) states of these clusters become degenerate with each other as the number of NH_3 molecules increases. With the aide of the theoretical calculations, this spectral change is ascribed to the dissociation of Na_3^- core in clusters. This may be the first observation of the dissolution of metal aggregates in small clusters.

I-P-2 Theoretical Study of $[Na(H_2O)_n]^-$ (n = 1–4) Clusters: Geometries, Vertical Detachment Energies and IR Spectra

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[*J. Phys. Chem. A* **104**, 3299 (2000)]

Geometries, vertical detachment energies (VDEs) and IR spectra of $[Na(H_2O)_n]^-$ (n = 1–4) have been investigated by ab initio MO method at correlated level. Water molecules are bound to Na^- via Na–H as well as hydrogen bond interactions. The calculated VDEs are in good agreement with the recent photoelectron spectroscopy and all observed bands are assignable to the $3^2S(Na)–3^1S(Na^-)$ and $3^2P(Na)–3^1S(Na^-)$ type transitions perturbed by hydration. They are shifted to higher energy with increasing n by keeping their separation almost unchanged, which reflects the hydration structure of Na^-. We also report the calculated IR spectra that are informative about the ionic Na–H bonds and the hydrogen-bond network among water molecules in the clusters.

I-P-3 Theoretical Study of $[Na(NH_3)_n]^-$ (n = 1–4)

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[*J. Chem. Phys.* **113**, 9540 (2000)]

In connection with the recent photoelectron spectroscopy of negatively charged Na atom in ammonia clusters, the geometries, electronic state, vertical detachment energies, and harmonic frequencies of $[Na(NH_3)_n]^-$ (n = 1–4) have been studied by *ab initio* MO method. Structure having as many Na–N bonds as possible becomes more stable than other isomers as n grows. The Na 3s electrons are widely spread and delocalized in space outside the $[Na(NH_3)_n]^+$ core for $n \geq 2$. The dramatic red-shifts of the photoelectron band for the 3^2P-type transition with increasing n reflect the electronic change from an atomic state to one-center Rydberg-like states in the neutrals. The frequencies of the combined vibrations of the NH_3 ν_1 mode are nearly degenerate and are expected to coalesce into only one strong IR band in the NH stretch region irrespective of n.

I-Q Theoretical Analyses on Nonlinear Behavior of Complex Systems

When material A and material B form a complex system, for example, an interface (or an interface region) newly appears between the two materials. Structure and properties of the interface are often totally different from those of the bulk materials, with the result that the complex system exhibits highly nonlinear behavior that can never be understood by superposition of the behaviors of the individual materials. We deal with a complex system in which liquid solvent or aqueous solution is one of the constituents. The integral equation theories are applied to the liquid solvent and combined with theoretical methods or computer simulation techniques for the other constituents. Some of the complex systems considered are biomolecules in aqueous solution, molecular assemblies formed by self-organization of surfactant molecules in solvent, metal-liquid interface, solvent-mediated interaction between colloidal particles, liquids at surfaces, and surface-induced phenomena.

I-Q-1 Peptide Conformations in Alcohol and Water: Analyses by the Reference Interaction Site Model Theory

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[*J. Am. Chem. Soc.* **122**, 2773 (2000)]

It is experimentally known that alcohol induces peptides to form α-helix structures much more than water. Though the α-helix structure formed is independent of the alcohol species, degree of the induction increases as bulkiness of the hydrocarbon group in an alcohol molecule increases. In this article we investigate conformations of peptides (Met-enkephalin and the C-peptide fragment of ribonuclease A) in methanol, ethanol, and water using the reference interaction site model theory. Molecular models are employed for the solvents. Our theoretical results show the following. Alcohol indeed facilitates peptide molecules to form the secondary structures with intramolecular hydrogen bonds such as the α-helix. In alcohol a solvophobic atom of a peptide is *less solvophobic* than in water while a solvophilic atom is *less solvophilic*. The solvation free energy in alcohol thus becomes considerably less variable against conformational changes than in water, with the result that the conformational stability in alcohol is governed by the conformational energy. The peptide molecule tends to take a conformation with the lowest conformational energy such as the α-helix, which is independent of the alcohol species. Moreover, these trends are enhanced as bulkiness of the hydrocarbon group in an alcohol molecule increases. In the text, the microscopic origin of the differences between alcohol and water in solvation of peptide molecules, which cannot be obtained by analyses treating the solvent as a dielectric continuum, is discussed in detail.

I-Q-2 Binary Fluid Mixture Confined between Macroparticles: Surface-Induced Phase Transition and Long-Range Surface Forces

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[*Chem. Phys. Lett.* **325**, 281 (2000)]

A binary fluid mixture of components 1 and 2, which is confined between two macroparticles separated by distance L, is analyzed by the RISM theory. Particles of component 1 interact through attractive potential, and those of component 2 and those of different components interact through hard-sphere potential. The macroparticle-fluid particle potential is the hard-sphere one. Component 2, the minor component, is enriched near each macroparticle. When the concentration of component 2 in the bulk Y_2 is sufficiently high, the following is observed. As L decreases component 2 is even more enriched in the confined domain, and at the threshold value L_T the theory exhibits a signal of the surface-induced phase transition, appearance of the second phase of component 2 in the confined domain. This phenomenon can occur even when the bulk mixture is stable as a single phase. As Y_2 increases L_T becomes larger. (L_T-d_M) can be far longer than the molecular scale, and the attractive interaction induced between macroparticles becomes correspondingly long range.

I-Q-3 Solvent Effects on Conformational Stability of Peptides: RISM Analyses

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[*J. Mol. Liq.* in press]

We describe features of our methodology for predicting tertiary structures (*i.e.*, conformations) of proteins in solvent just from the amino-acid sequences and molecular models for the solvent. The methodology, which is a combination of the Monte Carlo simulated annealing technique and the reference interaction site model theory, is illustrated for the small peptides, Met-enkephalin and C-peptide. Important roles played by water are discussed, and the alcohol effects on peptide conformations are newly analyzed.

I-Q-4 Effects of a Trace Amount of Hydrophobic Molecules on Phase Transition for Water Confined between Hydrophobic Surfaces: Theoretical Results for Simple Models

KINOSHITA, Masahiro
(Kyoto Univ. and IMS)

[*Chem. Phys. Lett.* **326**, 551 (2000)]

The author has analyzed the phase transition phenomenon for a hydrophilic fluid containing a hydrophobic component at low concentration, which is confined between hydrophobic surfaces, using the RISM-HNC theory with a simple model. Among various hydrophilic fluids, water is doubtlessly the most important one. Water molecules interact through strongly attractive potential, and apolar particles or hydrophobic molecules are soluble only at extremely low concentrations. However, presence of even a trace amount of those molecules affects the phase transition behavior to a drastic extent. Even when the surface separation is far larger than the molecular scale, the wetting of the hydrophobic molecules and the drying of water can occur in the domain confined. The attractive interaction induced between the surfaces become correspondingly long range. As the concentration of the hydrophobic component becomes higher, the wetting/drying transition occurs at a larger surface separation and the induced interaction becomes longer range. The hydrophobic molecules, which are contained in water within biological systems at very low concentrations, have caught little attention so far but should play essential roles in a variety of surface-induced phenomena.

I-Q-5 Methodology for Predicting Approximate Shape and Size Distribution of Micelles

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[*Stud. Surf. Sci. Catal.* in press]

We propose a methodology for predicting the approximate shape and size distribution of micelles with all-atom potentials. A thermodynamic theory is combined with the Monte Carlo simulated annealing technique and the reference interaction site model theory. Though the methodology can be applied to realistic models of surfactant and solvent molecules with current computational capabilities, it is illustrated for simplified models as a preliminary step.

I-R Electronic Structure of a Molecule in Solution

Chemical reaction is undoubtedly the most important issue in the theoretical chemistry, and the electronic structure is a key to solve the problem. As long as molecules in the gas phase are concerned, the theory for the electronic structure has been enjoying its great success. However, when it comes to molecules in solution, the stage of theory is still an infant. We have recently proposed a new method refereed to as RISM-SCF based on the integral equation theory of molecular liquids (RISM) and the ab initio electronic structure theory (SCF).[1)] The integral equation approach replaces the reaction field in the continuum models by a microscopic expression in terms of the site-site radial distribution functions between solute and solvent.

$$V_\lambda = \sum_j \int 4\pi r^2 \frac{q_j}{r} g_{j\lambda}(r)dr$$

where j and λ specify solvent and solute sites, respectively, and r denotes the solvent density. The site-site radial distribution functions $g_{\lambda j}(r)$ can be calculated from the extended RISM equation. Using V_λ the solvated Fock operator is defined as,

$$F^s = F^g - \sum_\lambda V_\lambda b_\lambda$$

where b_λ is a population operator of solute atoms. The statistical solvent distribution around solute is determined by the electronic structure or the partial charges of solute, while the electronic structure of solute is influenced by the solvent distribution. Therefore, the Hartree-Fock equation and the RISM equation should be solved in a self-consistent manner. It is this self-consistent determination of the solute electronic structure and the solvent distribution around the solute that features the RISM-SCF procedure.

The same Fock operator can be derived from a variation principle.[2)] Defining the Helmholtz free energy A as following;

$$A = E_{solute} + \Delta u$$

where E_{solute} is the energy of solute under solvent influence, and $\Delta\mu$ is the solvation free energy represented in terms of the Singer-Chandler formula. The Fock operator for a solute molecule in solvent as well as the RISM-HNC equations can be obtained as the first order variations with respect to the wave functions and the pair correlation functions under the constraint of the orthonormality to the molecular orbitals. The latest development along this line are reported below.

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I-R-1 Ab initio Study of Water: Liquid Structure, Electronic and Thermodynamic Properties over a Wide Range of Temperature and Density

SATO, Hirofumi; HIRATA, Fumio

[*J. Chem. Phys.* **111**, 8545 (1999)]

The electronic and liquid structures of water and its thermodynamic properties are studied over a wide range of temperature (0°–600 °C) and density (0.6–1.4 g/cm^3) based on the ab initio molecular orbital theory combined with the integral equation method of liquid. Unlike standard treatments of water by means of the classical statistical mechanics including molecular simulations, the effective charges on oxygen and hydrogen atoms in water molecules are not “input parameters,” but naturally predicted from the theory in the course of self-consistent determination of the electronic structure and the density pair correlation functions in liquids. It is found that the molecular dipole moments and electronic polarization energies decrease with increasing temperature and/or density. The theoretical results for dipole moments are in quantitative accord with the experimental data, which has been determined based on the NMR chemical shift coupled with the molecular dynamics simulation. The state dependence of the electronic structure is discussed in terms of the thermal activation of molecules and intermolecular interactions including the hydrogen bonds. The liquid structure of water is discussed in the wide range of thermodynamic states in terms of $S(r)$, an average response of the pair correlation functions to temperature change which is introduced in the present study in order to make structural characteristics of water more distinctive. It is concluded from the behavior of the function that the short range structure of water retains the characteristics to ice, or the tetrahedral configuration, over relatively wide range of temperature in the normal density (1.0 g/cm^3). The ice-like characteristics of water disappear to large extent both at high (1.4 g/cm^3) and low (0.6 g/cm^3) densities for different reasons: in the high density due to the packing effect, while in the low density due to essentially entropic cause, or increased configuration space available to a molecule. The distance between the nearest-neighbor molecules in water are insensitive to the density change compared with those corresponding to the Lennard-Jones fluid. The difference in the behaviors between the two fluids is explained in terms of the intermolecular interactions and liquid structures. The number of hydrogen bonds is calculated from the oxygen–hydrogen pair correlation function using a new definition based on $S(r)$, which enables us to distinguish the hydrogen-bonded OH pairs from those just in contact due to packing effect. The temperature and density dependence of the quantity is discussed in terms of the liquid structure of water.

I-R-2 Solvent Effects on a Diels-Alder Reaction in Supercritical Water: RISM-SCF Study

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[*J. Am. Chem. Soc.* **122**, 2289 (2000)]

A Diels-Alder reaction in supercritical water is studied by means of combined electronic structure and liquid state theories. The target system is the cycloaddition of cyclopentadiene with methyl vinyl ketone. The rate and the yield of the reaction in supercritical water are calculated and compared with those in ambient water. The activation free energies of the two isomers, cis and trans, are compared. The results are in agreement with the experimentally observed increase of the rate and the yield. The solvation effect for the rate constant is decreased in supercritical water, but the rate is increased because of the thermal excitation rather than the solvation effect. The trans-conformer has shown less activation energy in ambient water and supercritical water compared to the cis-conformer. The estimated yield in supercritical water is more than 600 times higher than in ambient water. The high yield in supercritical water is due to the high solubility of the reactants to supercritical water.

I-R-3 A Theoretical Study on a Diels-Alder Reaction in Ambient and Supercritical Water: Viewing Solvent Effects through Frontier Orbitals

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[*Chem. Phys.* **258**, 151 (2000)]

Solvent effects on the *endo/exo* selectivity of an asymmetric Diels-Alder reaction in ambient and supercritical water are studied by means of a combined electronic structure and liquid state theory. The target system is the cycloaddition of cyclopentadiene with methyl vinyl ketone. The rate constant and the equilibrium constant are obtained from the activation free energies and the free energy change of reaction for the two isomers. The results for the equilibrium constant are in qualitative agreement with the experimentally observed *endo/exo* selectivity. The relative rate constants show that the *endo* reaction occurs preferentially in wide range of thermodynamic conditions. Difference of the solvation free energy shows that *endo/exo* selectivity is enlarged in ambient water by hydrophobic effect and that it disappears completely in supercritical water. The theoretical results are analyzed in the light of the frontier orbital theory in order to aquire physical insight of solvent effects on the stereo-selectivity.

I-R-4 Self-Consistent Field, *Ab initio* Molecular Orbital and Three-Dimensional Reference Interaction Site Model Study for Solvation Effect on Carbon Monoxide in Aqueous Solution

SATO, Hirofumi; KOVALENKO, Andriy; HIRATA, Fumio

[*J. Chem. Phys.* **112**, 9463 (2000)]

We have developed a three-dimensional (3D) extension of the reference interaction site model-self-consistent field (RISM-SCF) method to treat the electronic structure of a solvated molecule. The site–site treatment of the solute–solvent correlations involving the approximation of radial averaging constitutes a bottleneck of the RISM-SCF method, and thus lacks a 3D picture of the solvation structure for complex solutes. To resolve this problem, we devised out a 3D generalization of the RISM integral equations which yields the 3D correlation functions of interaction sites of solvent molecules around a solute of arbitrary shape. In the present article, we propose a SCF combination of the ab initio molecular orbital (MO) methods and 3D-RISM approach. A benchmark result for carbon monoxide in ambient water is also presented.

I-R-5 Which Carbon Oxide is More Soluble? Ab initio Study on Carbon Monoxide and Dioxide in Aqueous Solution

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[*Chem. Phys. Lett.* **323**, 257 (2000)]

In disagreement with an intuitive prediction on the basis of the molecular size and dipole moment, it is observed empirically that the solubility of carbon dioxide (CO_2) in water is larger than that of carbon monoxide (CO). In order to shed light on this puzzling behavior, the solvation free energy of CO and CO_2 in aqueous solution is studied by means of the RISM-SCF/MCSCF method, a combined ab initio molecular orbital theory and statistical mechanics theory of molecular liquids. It is shown that the specific hydrogen bonding between oxygen atoms in CO_2 and water molecules makes CO_2 more soluble.

I-R-6 NMR Chemical Shifts in Solution: A RISM-SCF Approach

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[*Chem. Phys. Lett.* **325**, 668 (2000)]

The NMR chemical shift induced by solvation is formulated based on the ab initio electronic structure theory coupled with the integral equation method of molecular liquids. In order to examine the validity of the theory, the chemical shift of the atoms in a water molecule in water is calculated. The preliminary result with respect to hydrogen gives a reasonable account for the solvation shift, and for its temperature and density dependence.

I-R-7 ElectronL Self-Trapping in Two Dimensional Fluid

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[*Chem. Phys. Lett.* **326**, 199 (2000)]

The behavior of an excess electron in two dimensional classical liquid has been studied with the aid of Chandler, Singh and Richardson (CSR) theory [*J. Chem. Phys.* **81**, 1975 (1984)]. The size or dispersion of the wavepacket of a solvated electron is very sensitive to the interaction between the electron and fluid atoms, and exhibits complicated behavior in its density dependence. The behavior is interpreted in terms of an interplay among three causes: The excluded volume effect due to solvent, the pair attractive interaction between the electron and a solvent atom, and a balance of the attractive interactions from different solvent atoms.

I-S Solvation Thermodynamics of Protein and Related Molecules

Concerning biomolecules such as protein, it is a final goal for the biochemistry and biophysics to explore the relation between conformations and biological functions. The first important step toward the goal would be to explain the conformational stability of biomolecules in terms of the microscopic structure of the molecules in solvent. It is an extremely difficult problem by any means due to the overwhelmingly large degrees of freedom to be handled, including protein and solvent. As long as the small and/or short-time fluctuations of protein around the native structure is concerned, a variety of molecular simulation techniques provides a quite powerful tool to explore the microscopic structure of protein and solvent. However, the techniques are not so effective to characterize stability of the macromolecules in solution, to which the thermodynamic limit ($V \to \infty$, $N \to \infty$, with $V/N = const.$) is concerned. In such a case, methods based on the statistical mechanics of liquids should be natural choice for sampling configurations of solvent interacting biomolecules. The extended RISM theory is the most promising candidate of such methods, which provides not only solvation thermodynamics but also microscopic description at the level of the pair correlation functions.1) Obvious technical difficulties which one may face in applying the theory to such a large system are not only the computation time but also the stability of the numerical solution.2)

Here, we present our recent effort to tackle the problem using the two theoretical tools based on the statistical mechanics of liquids: The extended RISM and the scaled particle theories (SPT).3) The studies for the solvation thermodynamics of small molecules such as ions are also included because it is regarded as elementary processes for the solvation of biomolecules, and because it is prerequisite for studying the more complicated molecules.

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I-S-1 Salt Effect on Stability and Solvation Structure of Peptide: An Integral Equation Study

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[*Bull. Chem. Soc. Jpn.* **73**, 1113 (2000)]

Salt effects on the stability and on the solvation structure of a peptide in a variety of aqueous solutions of the alkali-halide ions are studied by means of the reference interaction site model (RISM) theory. The order of salt effect on the peptide stability is consistent with the experimental results; the order follows the Hofmeister series. The results are further analyzed in order to clarify the nature of the salt effect which determines the Hofmeister series and to find the reason why the Hofmeister series applies so generally to a variety of solutes in aqueous solutions. A heuristic model for explaining salt effects on the solvation structure of the peptide is proposed based on changes in the peptide-water pair correlation functions due to the ion perturbation.

I-S-2 Theoretical Study for Partial Molar Volume of Amino Acids in Aqueous Solution: Implication of Ideal Fluctuation Volume

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[*J. Chem. Phys.* **112**, 9469 (2000)]

A Kirkwood-Buff equation for the partial molar volumes of polyatomic molecules in solutions are derived based on the reference interaction site model (RISM) theory of molecular liquids. The partial molar volume of the twenty amino acids in aqueous solution at infinite dilution are calculated using the equation, and the results are discussed in comparison with the experimental data. The results indicate that ionizations of the C– and N–terminus groups give negative contributions to the volume ranging from –3.2 cm^3/mol to –9.7 cm^3/mol depending on the amino acid. Ionization of the dissociable residues also give negative contribution which ranges from –3.0 cm^3/mol to –6.0 cm^3/mol. On the other hand, contribution of the fractional charges on atoms to the volume is not necessarily negative, but rather slightly positive with few exceptions. It is clarified that contribution from an atom group to the volume is largely dependent on the situation where the group is placed. Therefore, it is concluded that the conventional way of determining the partial molar volume from group contributions is not reliable. The theoretical results for the partial molar volume exhibit a systematic deviation from corresponding experimental data, which increases nearly proportionally with increasing temperature and with the number of atoms in the amino acids. In order to account for the deviation, a concept of the "ideal fluctuation volume" is proposed, which is the ideal gas contribution to the volume, originating from the intra-molecular fluctuation of solute.

I-T Collective Density Fluctuations in Polar Liquids and Their Response to Ion Dynamics

As to the model for molecular diffusion in polar liquids, there are two quite different points of view. One is the conventional rot-translation model, and the other the interaction-site description which sees the diffusion of a molecule as a correlated motion of each atom (site).1) It is clearly advantageous to use the interaction-site description compared to the rot-translation model to account for chemical characteristics of solvent as well as solute dynamics. However, the interaction-site description has its own disadvantage in interpreting physical meaning of the results, since it does not give an explicit picture for the rotational relaxation of molecules, which can be directly probed by many experimental means including the dielectric and NMR relaxation. We have solved the problem by extracting collective modes of the density fluctuation from the site-site density correlation functions. In our recent study for dynamics of molecular liquids based on the interaction-site model, we have succeeded to abstract the collective excitations in liquids, which can be identified as optical and acoustic modes, by diagonalizing the collective frequency matrix appearing in the generalized Langevin equation. The two modes arise essentially from the rotational and translational motions of molecules.2) We applied the method to the ion dynamics in a dipolar liquid, and could have explained successfully the peculiar size dependence of friction of alkali and halide ions in terms of response of the collective excitations in solvent to the solute displacement.3)

In the past year, we have elaborated the memory kernel in our generalized Langevin equation base on the mode coupling theory. We have also extended our treatment to dynamics of water and hydrated ions. Those studies as well as other related topics are reviewed below.

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I-T-1 Relaxation of Average Energy and Rearrangement of Solvent Shells in Various Polar Solvents in Connection with Solvation Dynamics: Studied by RISM Theory

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[*Chem. Phys. Lett.* in press]

We employ a reference interaction-site model (RISM) theory to estimate the relaxation dynamics of average energy of solute-solvent systems as well as time-dependent radial distribution functions of solvents viewed from the solute. The theoretical results indicate that the rearrangement of the second solvent shell is about an order of magnitude slower compared with that of the first shell. We suggest that the slower relaxation of further solvent shells can play a significant role for the dynamic relaxation of the inhomogeneous spectral width, which has been observed in our previous experiments of the time-resolved hole-burning and fluorescence spectroscopy.

I-T-2 Importance of Acoustic Solvent Mode and Solute-Solvent Radial Distribution Functions in Solvation Dynamics: Studied by RISM Theory

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[*J. Chin. Chem.* in press]

We have applied the reference interaction-site model (RISM) theory to explain our experiments on solvation dynamics of laser dyes in polar organic solvents by means of the transient hole-burning and time-resolved fluorescence spectroscopy [K. Nishiyama and T. Okada, *J. Phys. Chem. A* **101**, 5729 (1997); **102**, 9729 (1998)]. The experiments show that the dynamic response function of the relaxation derived from the inhomogeneous spectral band-width of the solute–solvent system relaxes about an order of magnitude slower than that of average energy of the system. On the basis of our present theoretical prediction, we suggest that the relaxation dynamics of the spectral width might be mainly characterized by the solvent acoustic mode (translational motion) as well as the rearrangement of second plus further solvent shells.

I-U Liquid-Solid Interface

Due to recent progress in experimental techniques in the in situ measurements, the electrochemistry seems making a new epoch in understanding the chemical processes at electrode-solution interfaces. For examples, the scanning tunneling microscope (STM) applied to the interface has been revealing detailed atomic structure of the interface.1) The surface enhanced infrared absorption spectroscopy has provided detailed picture regarding the orientation of water molecules at the surface.2) The information in atomic level have been combined with the traditional techniques in the electrochemistry such as the cyclic voltammogram to provide more complete picture of electrode-solution interfaces. Obviously, the traditional descriptions using electric double layer models, which are based on the continuum models of solvent, mismatch the level of detailness attained by the recent experimental techniques.

Theoretical understanding of the interface has also made great progress in the last two decades, especially, in terms of solvent configuration near electrode surfaces.3) The progress has been mainly driven by two theoretical methods in the statistical mechanics of liquids: the molecular simulation and the integral equation methods. The two methods have reached consistent molecular pictures regarding reorganization of the water structure in the vicinity of the flat electrode surface. Latest topics in those approaches concern the electronic structure of electrode. The method features a self-consistent treatment of the liquid state and the electronic structure of the metal surface. Significance of such treatments will become more and more clear as the methods are extended to chemical reactions at the interface, which are primary motivation for the electrochemistry.

Although the integral equation methods have great advantage in the overall description of the electrode-solution interface both at phenomenological and molecular levels, the models which have been employed for the metal surface seems oversimplified considering the resolution attained by latest development in the experimental techniques stated above. Here, we propose a new approach for the electrode-solution interface based on the reference interaction site method (RISM) of liquids, which can handle both the structured metal surface and water in atomic level.

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I-U-1 Potentials of Mean Force of Simple Ions in Ambient Aqueous Solution. I. Three-Dimensional Reference Interaction Site Model Approach

KOVALENKO, Andriy; HIRATA, Fumio

[*J. Chem. Phys.* **112**, 10391 (2000)]

We adapt the three-dimensional reference interaction site model (3D-RISM) to calculate the potentials of mean force for ion–molecular solution as a difference between the chemical potential of solvation of a cluster of solutes and of individual ones. The method yields the solvation structure around the cluster of solutes in detail. The solvation chemical potential is obtained for the three-dimensional hypernetted chain (3D-HNC) closure as well as for its partial linearization (3D-PLHNC approximation). The solvation chemical potential is obtained in a closed analytical form for both the 3D-HNC and 3D-PLHNC closures. The 3D-RISM integral equations are solved by using the supercell technique. A straightforward supercell treatment of ionic solute in polar molecular solvent leads to a big error in the potential of mean force as well as the solvation chemical potential, which for simple ions in water amounts to about 35 kcal/mol. We elaborated corrections to the 3D-RISM integral equations, alleviating the artifact of the supercell periodicity with an accuracy of 0.05 kcal/mol or better and restoring the long-range asymptotics of the solute–solvent correlation functions. The dielectrically consistent siteˆsite RISM/HNC theory (DRISM/HNC) is employed for the solvent correlations to provide a proper description of the dielectric properties of solution. This allowed us to extend the description to solution at a finite salt concentration. We converge both the 3D-RISM and site–site DRISM integral equations by using the method of modified direct inversion in the iterative subspace.

Owing to the proper initial guess of the correlation functions, iteration begins at once for a given temperature and full molecular charge, avoiding a gradual decrease of the temperature and increase of the site charges, which greatly reduces the computation time. We calculate and discuss the potentials of mean force for sodium chloride in ambient water at infinite dilution as well as at a finite concentration.

I-U-2 Potentials of Mean Force of Simple Ions in Ambient Aqueous Solution. II. Solvation Structure from the Three-Dimensional Reference Interaction Site Model Approach, and Comparison with Simulations

KOVALENKO, Andriy; HIRATA, Fumio

[*J. Chem. Phys.* **112**, 10403 (2000)]

We applied the three-dimensional reference interaction site model (3D-RISM) integral equation theory with the 3D hypernetted chain (3D-HNC) closure or its partial linearization (3D-PLHNC) to obtain the potentials of mean force (PMFs) and the solvation structure of sodium chloride in ambient water. The bulk solvent correlations are treated by the dielectrically consistent site–site RISM/HNC theory (DRISM/HNC) to provide a proper description of the dielectric properties of solution and to include the case of a finite salt concentration. The PMF is calculated as a difference in the solvation free energy of an ion pair and of individual ions. We obtained and analyzed in detail the PMFs and solvation structure for ion pairs of NaCl at infinite dilution and a concentration of 1 M. The results are in reasonably good agreement with molecular dynamics simulations for the same model of the solution species. Positions and orientations of water molecules in the first solvation shell around the ion pair are deduced. The short-range hydration structure of the ion pairs at infinite dilution and at moderate concentration is very similar. Ionic ordering and clustering is found in 1 M solution.

I-U-3 Hydration Free Energy of Hydrophobic Solutes Studied by a Reference Interaction Site Model with a Repulsive Bridge Correction and a Thermodynamic Perturbation Method

KOVALENKO, Andriy; HIRATA, Fumio

[*J. Chem. Phys.* **113**, 2793 (2000)]

We modify the site–site as well as three-dimensional (3D) versions of the reference interaction site model (RISM) integral equations with the hypernetted chain (HNC) closures by adding a repulsive bridge correction (RBC). The RBC treats the overestimation of water ordering around a hydrophobic solute in the RISM/HNC approximation, and thus refines the entropic component in the hydration free energy. We build up the bridge functions on r^{-12} repulsive core potentials, and propose RBC expressions for both the site–site and 3D-RISM approaches. To provide fast calculation, we obtain the excess chemical potential of hydration by using the thermodynamic perturbation theory (TPT). The site–site RISM/HNC+RBC as well as 3D-RISM/HNC+RBC approaches are applied to calculate the structure and thermodynamics of hydration of rare gases and alkanes in ambient water. For both approaches, the RBC drastically improves the agreement of the hydration chemical potential with simulation data and provides its correct dependence on the solute size. For solutes of a nonspherical form, the 3D treatment yields the hydration structure in detail and better fits simulation results, whereas the site–site approach is essentially faster. The TPT approximation gives the hydration thermodynamics in good qualitative agreement with the exact results of the thermodynamic integration, and substantially reduces computational burden. The RBC-TPT approximation can improve the predictive capability of the hybrid algorithm of a generalized-ensemble Monte Carlo simulation combined with the site–site RISM theory, used to describe protein folding with due account for the water effect at the microscopic level. The RBC can be optimized for better fit to reference simulation data, and can be generalized for solute molecules with charged groups.

I-U-4 Liquid Structure at Metal Oxide-Water Interface: Accuracy of a Three-Dimensional RISM Methodology

SHAPOVALOV, Vladimir[1]; TRUONG, Thanh N.[1]; KOVALENKO, Andriy; HIRATA, Fumio
([1]Univ. Utah)

[*Chem. Phys. Lett.* **320**, 186 (2000)]

We calculated the structure of water in contact with the MgO 100 surface by using the three-dimensional reference interaction site model 3D-RISM integral equation theory. The spatial distributions of water oxygen and hydrogen over the surface unit cell are calculated and discussed. The water density profiles and the orientations obtained are in good agreement with computer simulations for the same model of the interface. The 3D-RISM approach shows considerable promise as a constituent of a self-consistent description of chemical processes at a metal oxide–water interface.

I-U-5 Self-Consistent, Kohn-Sham DFT and Three-Dimensional RISM Description of a Metal –Molecular Liquid Interface

KOVALENKO, Andriy; HIRATA, Fumio

[*J. Mol. Liq.* in press]

We have developed a self-consistent description of a metal–molecular liquid interface by combination of the Kohn-Sham density functional theory (KS DFT) for the electronic density, and the three-dimensional reference interaction site model (3D RISM) integral equation theory for the classical site distribution profiles of molecular liquid. The electron and classical subsystems are coupled in the mean field approximation. The classical potentials of the metal acting on species of the liquid are taken in the linear response regime. Many-body effects of dense liquid on metal valence electrons are allowed for by averaging pseudopotentials of liquid molecules over the site distributions of liquid. The coupled KS DFT and 3D RISM equations are solved simultaneously by using the procedure of dynamic relaxation. The proposed approach is substantially less time-consuming as compared to a Car-Parrinello type simulation. A partial linearization of the hypernetted chain (PLHNC) closure to the RISM equation is proposed. The calculation is performed in the supercell technique for water at normal conditions in contact with the (100) FCC slab of a metal roughly modeled after copper. The results are in good agreement with the Car-Parrinello simulation for the same model. Further applications of the method proposed are discussed.

I-V Dimensional Crossovers and Excitation Spectra in Quasi-One-Dimensional Organic Conductors

In molecular materials including organic conductors and metal complexes, physical properties sensitively depend on electronic dimensionality, which is controlled by applying external or chemical pressure. Dimensional crossovers are classified according to whether one- or two-particle coherence in directions perpendicular to the highest conductivity is first restored by increasing dimensionality. The restoration of coherence depends on the asymptotic property of the corresponding one-dimensional system. For a one-dimensional gapless phase, interchain hopping easily restores the transverse one-particle coherence. If any excitation spectrum has a gap owing to electron correlation, the transverse one-particle process is so strongly suppressed that the transverse two-particle coherence is relatively easily restored. In quasi-one-dimensional organic conductors $(TMTTF)_2X$, the charge gap suppresses the transverse one-particle coherence and the antiferromagnetic transition takes place from a charge-localized phase. Even in the gapless phase of $(TMTSF)_2X$, effective dimensionality of the optical property is lowered by increasing energy scale. In mixed crystals $(DI\text{-}DCNQI)_2Ag_{1-x}Cu_x$ and $(DMe\text{-}DCNQI)_2Li_{1-x}Cu_x$, random potential scattering causes complex competition among the Mott-insulator, Anderson-insulator, and Fermi-liquid phases.

I-V-1 Quantum Phase Transitions and Collapse of the Mott Gap in the $d = 1 + \varepsilon$ Dimensional Hubbard Model with $2k_F$ Umklapp Scattering

KISHINE, Jun-ichiro

[*Phys. Rev. B* **62**, 2377 (2000)]

We study the low-energy asymptotics of the $d = 1 + \varepsilon$ dimensional Hubbard model with a circular Fermi surface where there is $2k_F$ umklapp scattering present *a priori*. Peculiarity of the $d = 1 + \varepsilon$ dimensions is incorporated through the imbalance between the elementary particle-particle and particle-hole (PH) loops: infrared logarithmic singularity of the PH loop is smeared for $\varepsilon > 0$. The one-loop renormalization-group flows indicate that a quantum phase transition from a metallic phase to the Mott insulator phase occurs at a finite on-site Coulomb repulsion U for $\varepsilon > 0$. We also discussed effects of randomness and obtained phase diagrams in terms of d, U, and strength of random backward scattering.

I-V-2 One– and Two–Band Hubbard Models in $d = 1 + \varepsilon$ Dimensions: Dimensionality Effects on the Charge and Spin Gap Phases

KISHINE, Jun-ichiro

[*J. Phys. Chem. Solids* in press]

To examine dimensionality effects on the charge/spin gap phases in quasi-one-dimensional, strongly correlated chain/ladder systems, we perform the one-loop renormalization-group analysis of the one- and two-band Hubbard models with circular Fermi surfaces in $d = 1 + \varepsilon$ dimensions. The renormalization-group flows indicate that raising dimensionality suppresses the charge and spin gap in the one and two-band cases, respectively. This result gives a clue to understand experimental indication: both the charge gap in the quasi-one-dimensional organic conductor $(TMTTF)_2Br$ and the spin gap in the doped ladder system $(Sr_2Ca_{12}Cu_{24}O_{41})$ are suppressed upon increasing pressure.

I-V-3 Interplay of Randomness, Electron Correlation, and Dimensionality Effects in Quasi-One-Dimensional Conductors

KISHINE, Jun-ichiro; YONEMITSU, Kenji

[*Phys. Rev. B* **62**, in press (2000)]

We study the interplay of randomness, electron correlation, and dimensionality effects in weakly coupled half-filled Hubbard chains with weak quenched random potentials, based on the renormalization-group (RG) approach. We perform a two-loop RG analysis of an effective action derived by using the replica trick, and examine the following crossovers and phase transitions from an incoherent metal regime: (1) a crossover to the Anderson localization regime, (2) an antiferromagnetic phase transition, and (3) a crossover to the quasi-one-dimensional weak-localization regime. The case of $d = 1 + \varepsilon$ $(\varepsilon \ll 1)$ dimensions is also mentioned. Based on the result, we tried a simple simulation of the experimentally suggested successive crossovers [antiferromagnetic, Anderson localization to metallic phases] upon doping in $(DI\text{–}DCNQI)_2Ag_{1-x}Cu_x$.

I-V-4 Charge Gap and Dimensional Crossovers in Quasi-One-Dimensional Organic Conductors

YONEMITSU, Kenji; KISHINE, Jun-ichiro

[*J. Phys. Chem. Solids* in press]

Quasi-one-dimensional quarter-filled organic conductors, $(TMTTF)_2X$ and $(TMTSF)_2X$, show a dimensional crossover, and their electronic properties change accordingly. We describe this using the two-loop perturbative and density-matrix renormalization-group methods, the ε expansion around one dimension, and the random phase approximation. The effect of dimerization on the charge gap and interchain one-particle coherence is clarified. The effect of random potentials is also studied to describe Mott insulator, Anderson localization, and metallic phases of $(DCNQI)_2Ag_{1-x}Cu_x$ mixed crystals.

I-V-5 Dimensionality Effects on the Charge Gap in the Dimerized Hubbard Model at Quarter Filling: the Density-Matrix and Perturbative Renormalization-Group Approaches

YONEMITSU, Kenji; KISHINE, Jun-ichiro

[*J. Phys. Soc. Jpn.* **69**, 2107 (2000)]

We study dimensionality effects on the charge gap in the dimerized Hubbard model at quarter filling, with two approaches. First, we examine three chains coupled via the interchain one-particle hopping integral t_b, by the density-matrix renormalization-group (DMRG) method. Next, we consider the $d = 1 + \varepsilon$ dimensional model, using the perturbative renormalization-group (PRG) method. The dimensionality is controlled through t_b and ε, respectively. Both approaches lead to the conclusion that, for a finite dimerization ratio, the charge gap decreases as the dimensionality increases.

I-V-6 Intra- and Inter-Chain Dynamic Response Functions in Quasi-One-Dimensional Conductors

YONEMITSU, Kenji

[*Synth. Met.* in press]

Intra- and inter-chain excitation spectra are studied in a spinless fermion model on a two-leg ladder at half filling. Numerical results are obtained by application of the density-matrix renormalization-group technique to the quantum transfer matrix for infinite systems. Near the metal-insulator transition, the intra-chain Coulomb repulsion is found to affect local current correlations more sensitively in the rung direction than in the leg direction.

I-W Optical Excitations in Charge-Lattice-Ordered Phases of One-Dimensional Materials

Halogen-bridged binuclear metal complexes, which are often called MMX chains, have strong electron-lattice coupling and electron-electron interaction. Various charge and lattice ordering phases are found and depend on the ligand, the halogen ion and the counter ion. An alternate-charge-polarization phase is observed as well as a metallic phase for the ligand dta. Meanwhile, for the ligand pop, an averaged-valence Mott-insulator phase and a charge-polarization phase are observed as well as a well-known charge-density-wave phase. The competition among these electronic phases is qualitatively understood in a model with strong on-site repulsion, two types of electron-lattice couplings, and two types of elastic couplings. However, the optical properties sensitively depend on the long-range part of the electron-electron interaction. To explain both static and dynamical properties, we add nearest- and next-nearest-neighbor repulsion terms to the model in order to discuss the stability of each phase from the strong-coupling viewpoint and clarify the origin of each peak in the optical conductivity spectrum.

I-W-1 Charge Ordering and Lattice Modulation in Quasi-One-Dimensional Halogen-Bridged Binuclear Metal Complexes

KUWABARA, Makoto; YONEMITSU, Kenji

[*Mol. Cryst. Liq. Cryst.* **343**, 47 (2000)]

We have investigated ground state phase diagrams of the MMX chains in a one-dimensional dimerized 3/4-filled model by exactly diagonalizing 12-site clusters. In charged chains where counter ions are present, competition occurs among a uniform state, a charge-density-wave (CDW) state and a charge-polarization (CP) state. Experimentally observed phases are understood by strengths of a site-diagonal electron-lattice coupling β, the interdimer transfer integral t_{MXM}, and an elastic constant, whose variation is roughly estimated from the inter-atomic spacing, the species of the halogen ion. The CP state is relatively stable for small t_{MXM} and the CDW state for large β. In neutral chains where counter ions are absent, the dimer units can move almost freely. Dimers are alternately shifted to form tetramers because of a strong off-diagonal electron-lattice coupling, thus stabilizing an alternate-charge-polarization (ACP) state.

I-W-2 Charge Ordering and Lattice Modulation in MMX Chains

KUWABARA, Makoto; YONEMITSU, Kenji

[*J. Phys. Chem. Solids* in press]

Ground state phase diagrams for the MMX chains are studied in a one-dimensional two-band model by exactly diagonalizing 18-site clusters. Qualitative behavior of the phase diagrams is explained by the strong-coupling expansion. The relative stability between the charge-density-wave (CDW) and charge-polarization (CP) states observed in charged chains is determined by the kinetic energy gain through second-order processes with respect to intra-dimer charge transfer. Thus the relative stability is ascribed to competition between on-site Coulomb repulsion U and a diagonal electron-lattice coupling (β). The CP state is relatively stable for strong U and the CDW for strong β. In neutral chains, an alternate-charge-polarization (ACP) state is always more stable than the CP state by the energy gain through fourth-order processes with respect to interdimer transfer.

I-W-3 Charge Ordering and Optical Conductivity of MMX Chains

KUWABARA, Makoto; YONEMITSU, Kenji

[*Proc. LLD2K* submitted]

We study the optical conductivity of the halogen-bridged binuclear metal complexes, using a one-dimensional dimerized 3/4-filled-band model and the Lanczos method. The spectra are quite sensitive to the charge ordering pattern and the long-range Coulomb interaction. For instance, in a charge-polarization (CP) state two peaks are generally expected and ascribed to intra-dimer and interdimer charge excitations when long-range interactions are taken into account. However, when the interdimer Coulomb repulsion is weaker than the intra-dimer repulsion, only a single peak may be observed because the oscillator strength of the interdimer charge excitation is much weaker than that of the intra-dimer one. We clarify relations between the various ordering states and their optical conductivity spectra and compare them with experimental results.

I-W-4 Charge Excitations in an Alternate Charge Polarization Phase of a One-Dimensional Two-Band Extended Peierls-Hubbard Model for MMX Chains

KUWABARA, Makoto; YONEMITSU, Kenji

[*Synth. Met.* in press]

We investigate the optical conductivity of a halogen-bridged binuclear metal complex in an alternate-charge-polarization phase observed in $Pt_2(dta)_4I$ below 80 K, using a one-dimensional two-band extended Peierls-Hubbard model and the Lanczos technique, to study the dependence of three main peaks ascribed to intra-dimer, interdimer and halogen(X)-to-metal(M) charge excitations on model parameters. We show that effective energy difference between the M(Pt)-d_{z^2} and X(I)-p_z orbitals (Δ_{eff}) must be small in order to reproduce the optical conductivity spectra observed experimentally. Here Δ_{eff} is defined as $\Delta + U_M - U_X + 2V_{MM} - 2V_{MX}$, where Δ is the bare level difference, U_M (U_X) the on-site Coulomb repulsion at M (X) site, and V_{MM} (V_{MX}) the nearest-neighbor repulsion within a dimer (between M and X sites).

I-W-5 Highly Doped Nondegenerate Conjugated Polymers—A Theory Using the DMRG Method

SHIMOI, Yukihiro[1]; KUWABARA, Makoto; ABE, Shuji[1]
([1]*Electron. Tech. Lab.)*

[*Synth. Met.* in press]

Highly doped conjugated polymers with a non-degenerate ground state are investigated theoretically by using the density-matrix renormalization-group method. We pointed out a crossover between polaron- and bipolaron-lattice via formation of polaron-pairs. We also indicate that, at high doping concentration, the gaps in charge and spin excitations become negligibly small, while the bond alternation still survives.

I-X Magnetic and Optical Properties of Two-Dimensional Metal-Complex and Organic Conductors

Assembled metal complexes $Et_nMe_{4-n}Z[Pd(dmit)_2]_2$ are two-dimensional electronic materials and show rich phases including paramagnetic-insulator, antiferromagnetic–insulator, superconductor and metallic phases in different temperature and pressure regions and with different cations. The variety comes from the presence of HOMO and LUMO bands near the chemical potential and from strong dimerization of $Pd(dmit)_2$ molecules. The dependence of the ground state on the cation $Et_nMe_{4-n}Z$ was roughly interpreted on the Hückel basis and is now understood from the strong-coupling viewpoint, which enables us to show the correlation between the transport and magnetic properties and the stability criterion of the antiferromagnetic phase. On the other hand, two-dimensional organic conductors θ-$(BEDT\text{-}TTF)_2X$ have no or very weak dimerization, so that the long-range part of the electron-electron interaction causes charge ordering and consequently insulator phases with different magnetic properties. The charge-ordering and magnetic-coupling patterns are understood on the basis of the anion-dependent anisotropy of Coulomb repulsion strengths and transfer integrals. Some of the optical properties may indicate importance of electron-phonon interaction as well, so that both static and dynamical properties are studied in a consistent manner.

I-X-1 Collective Excitations around Charge Ordered States and Coexistent States with Different Orders

MORI, Michiyasu; YONEMITSU, Kenji

[*Mol. Cryst. Liq. Cryst.* **343**, 221 (2000)]

Some novel ground states have recently been studied in molecular conductors. One is the coexistence of a spin density wave (SDW) and a charge density wave (CDW) in $(TMTSF)_2PF_6$, which is quasi-one-dimensional and is basically a quarter-filled system with dimerization. Seo and Fukuyama[1)] and Kobayashi *et al.*[2)] have used the Hartree approximation for one-dimensional extended Hubbard models and found coexistence of a $2k_F$ SDW with a $4k_F$ CDW and that with a $2k_F$ CDW, respectively. They claim that not only the on-site but also the nearest neighbor and the next-nearest-neighbor repulsive interactions are important, respectively. We study collective excitation spectra of such states with different orders. The excited states are calculated in the random phase approximation for the one-dimensional extended Hubbard model at quarter filling. In the charge ordered state, a dominant excitation in the current-current correlation function has no charge density modulation. A dominant excitation in the charge uniform state originates from crossing the dimerization gap and modulates the charge density.

References

1) H. Seo and H. Fukuyama, *J. Phys. Soc. Jpn.* **66**, 1249 (1997).
2) N. Kobayashi, M. Ogata and K. Yonemitsu, *J. Phys. Soc. Jpn.* **67**, 1098 (1998).

I-X-2 Anisotropic Collective Excitations around Various Charge Ordering States

MORI, Michiyasu; YONEMITSU, Kenji

[*J. Phys. Chem. Solids* in press]

Among the family of $(ET)_2X$ (ET = BEDT-TTF), the θ-type salts have no evident dimeric structure and no antiferromagnetic insulating phase near the superconducting phase in contrast to the κ-type salts. In the paramagnetic insulating phase, charge ordering (CO) states are observed by the X-ray studies.1) We notice that the various CO states are indeed possible and the intersite repulsive interactions are important in the θ-type salts. It is still hard to distinguish the ground states among many CO candidates in the actual salts. We calculate absorption spectra for various charge ordering (CO) states in the two-dimensional extended Hubbard model at quarter filling with the random phase approximation. Each CO state has its own characteristic and anisotropic excitations. In principle, these features should be observed in the optical measurements and tell which CO state is realized in the θ-$(ET)_2X$ salts.

Reference

1) M. Watanabe, Y. Nogami, K. Oshima, H. Mori and S. Tanaka, *J. Phys. Soc. Jpn.* **68**, 2654 (1999).

I-X-3 Stability and Cation Dependence of Magnetic Orders in $(Et_nMe_{4-n}Z)[Pd(dmit)_2]_2$

MORI, Michiyasu; YONEMITSU, Kenji

[*Synth. Met.* in press]

Electronic states of $(Et_nMe_{4-n}Z)[Pd(dmit)_2]_2$ (Z = P, As, Sb) depend on the cations, although they are isostructural and have little differences in the lattice parameters. The experimentally observed Néel temperature is about 30 K for Me_4P and 18 K for Me_4Sb and Et_2Me_2P. For Et_2Me_2Sb, the antiferromagnetic (AF) phase transition is not observed above 5 K by the ESR measurement.1) The cation dependence of the magnetic phase transitions in the $Pd(dmit)_2$ salts is studied by calculating effective exchange interactions between spins on dimers in a two-band Hubbard model. The effective Hamiltonian in the low-energy region is reduced to a spin-1/2 AF Heisenberg model on the anisotropic triangular lattice. The existence/absence of the magnetic order is understood from the sublattice magnetization calculated within the linear spin wave theory, as shown in Figure 1. For Et_2Me_2Sb, the AF order is destroyed by magnetic frustration.

Reference

1) T. Nakamura, H. Tsukada, T. Takahashi, S. Aonuma and R. Kato, *Mol. Cryst. Liq. Cryst.* **343**, 187 (2000).

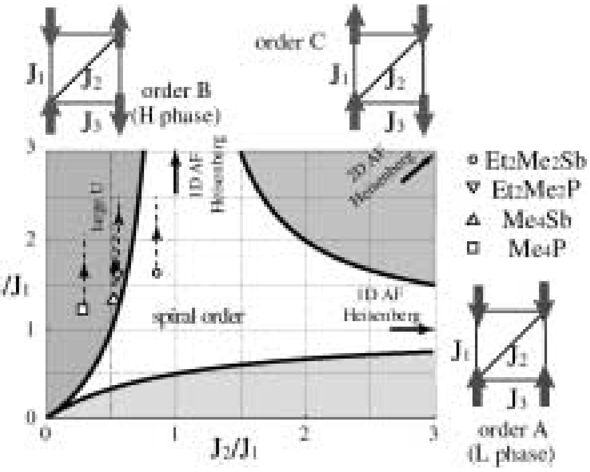

Figure 1. Magnetic phase diagram in the linear spin wave theory for the orders A, B and C. In each shaded region, the displayed magnetic order is stable. The salts with different cations are roughly located on the dashed lines. The position moves upward along the J_3/J_1 axis, as the on-site repulsive interaction is strengthened.

I-Y Multi-Phase Stability and Nonlinear Dynamics near Phase Boundary

In organic donor-acceptor compounds showing a neutral-ionic structural phase transition, each phase is locally stable and separated by a potential barrier from the other phase. To study photoinduced cooperative phenomena and dynamical processes, the high-energy part of the many-body potential is studied as well as the local minima. Techniques developed in molecular dynamics may be useful for such evolution of many-electron states. In conducting polymers possessing a non-degenerate bond-ordered ground state, electroluminescence involves recombination of excitons or polarons, which are produced by nonlinear processes of coupling between many electrons and phonons. Linear excitation analysis around such quasiparticles is useful to compare with experimental data.

I-Y-1 Influence of Short-Range Interference on Ionization Threshold Law

MIYASHITA, Naoyuki[1]; WATANABE, Shinichi[2]; MATSUZAWA, Michio[2]; MACEK, Joseph H.[3]
([1]GUAS; [2]Univ. Electro-Commun.; [3]Univ. Tennessee)

[*Phys. Rev. A* **61**, 14901 (2000)]

Electron-impact ionization of the collinear $Z = 1/4$ model atom is investigated in order to examine a nonclassical behavior of the ionization cross sections. Slightly above the ionization threshold, ab initio calculations reveal a distinctive dip due to short-range dynamics. The dip is a strongly energy-dependent feature in the usually smooth and structureless ionization cross section and is foreign to treatments based on classical, as well as semiclassical mechanics. The $Z = 1/4$ model thus serves as a counterexample to the standard Wannier treatment of near-threshold ionization. The hyperspherical hidden-crossing theory is applied to identify the origin of the dip.

I-Y-2 Potential Analysis for Neutral-Ionic Phase Transition

MIYASHITA, Naoyuki[1]; YONEMITSU, Kenji
([1]GUAS)

Adiabatic potentials around neutral and ionic phases are studied in two-site and four-site extended-Hubbard models with varying energy difference between donor and acceptor sites. Mean-field solutions are searched under the constraints that the spin-density alternation amplitude and the degree of charge transfer take some fixed values. Unstable regions are numerically hard to access, so that we develop several iteration schemes.

I-Y-3 Localized Vibrational Modes of Excitations in Electroluminescent Polymers

JIANG, Hao[1]; XU, Xiao-hua[1]; SUN, Xin[1,2]; YONEMITSU, Kenji
([1]Fudan Univ.; [2]Natl. Lab. Infrared Phys.)

[*Chin. Phys. Lett.* **16**, 836 (1999)]

The localized vibrational modes of an exciton and a polaron are investigated, and the results show that the frequencies of the three even parity modes of the exciton are very different from those of the polaron. For the exciton, three modes are distinctly separated, but, for the polaron, two modes with higher frequencies are close to each other. Then, it is possible to distinguish an exciton from a polaron by watching their Raman spectra. Therefore, the localized modes may be used to specify the exciton and the polaron in electroluminescent polymers.

I-Y-4 Photoinduced Polarization Inversion in a Polymeric Molecule

SUN, Xin[1,2]; FU, Rouli[2]; YONEMITSU, Kenji; NASU, Keiichiro[3]
([1]Fudan Univ.; [2]Natl. Lab. Infrared Phys.; [3]Inst. Mater. Struct. Sci.)

[*Phys. Rev. Lett.* **84**, 2830 (2000)]

The polymeric molecule can exhibit a new photoinduced phenomenon where the electric dipole of the molecule with a bipolaron is reversed by absorbing one photon. This photoinduced polarization inversion occurring in a single molecule is an ultrafast process with a relaxation time of 200 fs.