RESEARCH ACTIVITIES I
Department of Theoretical Studies

I-A 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-A-1 Multicanonical Monte Carlo Simulation of a Small Peptide in Aqueous Solution Based on the RISM Theory

MITSUTAKE, Ayori[1]; KINOSHITA, Masahiro[2]; OKAMOTO, Yuko; HIRATA, Fumio
([1]Keio Univ.; [2]Kyoto Univ.)

We report the results of multicanonical Monte Carlo simulation of a penta peptide, Met-enkephalin, in aqueous solution that is based on the reference interaction site model theory. Averages of the energy functions, end-to-end distance, dihedral-angle distributions, and radial distribution functions are calculated as functions of temperature from a single simulation run. This is accomplished by the single-histogram reweighting techniques. It is shown that the peptide is almost fully extended in aqueous solution at all temperatures, while it forms β-turn structures in gas phase at low temperatures.

I-A-2 Replica-Exchange Multicanonical and Multicanonical Replica-Exchange Monte Carlo Simulations of a Small Peptide

MITSUTAKE, Ayori[1]; SUGITA, Yuji; OKAMOTO, Yuko
([1]Keio Univ.)

We recently developed the replica-exchange multicanonical algorithm and the multicanonical replica-exchange method for molecular dynamics simulations. In the first method, one first estimate the multicanonical weight factor from a short replica-exchange simulation, using the multiple-histogram reweighting techniques. One then performs a long multicanonical production run. The second method is a further extension of the first in which a replica-exchange production simulation is performed with each replica in multicanonical ensemble. In this article, we develope Monte Carlo versions of the two methods and show that these algorithms are very effective for simulations of a small peptide.

I-A-3 Examination of Parallel Simulated Annealing Using Genetic Crossover

HIROYASU, Tomoyuki[1]; MIKI, Mitsunori[1]; OGURA, Maki[1]; OKAMOTO, Yuko
([1]Doshisha Univ.)

This paper proposes Parallel Simulated Annealing using Genetic Crossover (PSA/GAc). In this algorithm, there are several processes of Simulated Annealing (SA) working parallel. To exchange information between the solutions, the operation of genetic crossover is performed. Through the continuous test problems, it is found that PSA/GAc can search the solution effectively. The proposed algorithm is also applied to the prediction of protein tertiary structure. Comparing PSA/GAc to the conventional algorithm, it is also found that PSA/GAc is an effective algorithm for real world problems.

I-A-4 Solvent Effects on the Free Energy Landscape of a Short Peptide

SUGITA, Yuji; OKAMOTO, Yuko

We have studied the effects of solvent on the free energy landscape of a short peptide, Met-enkephalin, by carrying out the molecular dynamics simulations both in vacuum and in aqueous solution with explicit water molecules. The replica-exchange multicanonical algorithm, which has been recently developed by us, was employed to sample a wide conformational space. The results of the simulations were analyzed by the histogram reweighting techniques and principal component analyses. By comparing the free energy landscape in water with that in vacuum, we found that the free energy landscape is significantly changed by the solvent effects. The dependence of the free energy landscape on the different force fields is also discussed.

I-A-5 Comparison of the Numerical Efficiency of Three New Generalized-Ensemble Algorithms for Conformational Sampling of a Peptide in Explicit Water

SUGITA, Yuji; OKAMOTO, Yuko

In many systems with rough energy landscape, the conventional molecular dynamics or Monte Carlo simulation tends to get trapped in local-minimum states and cannot sample wide configurational space. To overcome this difficulty, we have recently developed two new algorithms, namely, replica-exchange multicanonical algorithm and multicanonical replica-exchange method. In this article, we compare the numerical efficiency of these methods with that of the original replica-exchange method in simulations of a peptide with a number of explicit water molecules. We employed the average tunneling time in the energy space as a measure of the sampling efficiency. It has been shown that the sampling efficiency of the new algorithms becomes much greater than that of the original replica-exchange method.

I-B 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-B-1 Generalized-Ensemble Simulations for Systems with First-Order Phase Transition

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MITSUTAKE, Ayori[1]; OKAMOTO, Yuko
([1]Keio Univ.)

Replica-exchange method is a powerful generalized-ensemble algorithm that can alleviate the difficulty of getting trapped in states of energy local minima. The method, however, fails for systems with first-order phase transition. In this article we show that the recently developed algorithms, replica-exchange multicanonical algorithm and multicanonical replica-exchange method, can be successfully applied to systems with first-order phase transition. We present our results, taking the example of the two-dimensional 10-state Potts model.

I-B-2 Li_8 Cluster Structures Studied by *Ab Initio* Replica-Exchange Monte Carlo Method

NISHIKAWA, Takeshi[1]; SUGITA, Yuji;
OKAMOTO, Yuko; ISHIKAWA, Yasuyuki[2]
([1]AIST; [2]Univ. Puerto Rico)

Interest in metal, semiconductor, and molecular clusters has been growing explosively in the past two decades due to the experimental advances that have facilitated the study of clusters. Furthermore, theoretical advances have enhanced the ability to interpret experimental results. Still lacking is the ability to routinely determine the structures of clusters. In the previous work, *ab initio* replica-exchange Monte Carlo method was developed and implemented to determine the global and local minimum configurations of Li_6 clusters. Gaussian98 was used for the calculations of the electronic structures. In this work, we discuss results of replica-exchange Monte Carlo simulations of Li_8 clusters.

I-C Theoretical Studies of Chemical Reaction Dynamics

I-C-1 Quantum Reaction Dynamics of O(^3P) + HCl on a New *ab initio* Potential Energy Surface

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

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

Quantum reaction dynamics of O(^3P) + 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-Gordon (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-C-2 Quantum-Classical Correspondence in the O(^3P) + HCl and Cl(^2P) + OH Reactions for Total Angular Momentum $J = 0$

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

[*J. Chem. Phys.* **114**, 1549 (2001)]

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(^3P) + HCl reaction and the reverse reaction Cl(^2P) + OH. The S4 potential surface, which is based on MRCI+Q/cc-pVTZ energies scaled by the scaled external correlation method [B. Ramachandran *et al.*, *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-C-3 Cumulative Reaction Probability and Reaction Eigenprobabilities from Time-Independent Quantum Scattering Theory

TOLSTIKHIN, Oleg I.[1]; OSTROVSKY, Valentin N.[2]; NAKAMURA, Hiroki
([1]IMS and Kurchatov Inst.; [2]IMS and Univ. St. Petersburg)

[*Phys. Rev. A* **63**, 042707 (2001)]

The cumulative reaction probability (CRP) is a gross characteristic of rearrangement collision processes defining the reaction rate constant. This paper presents a complete development of the approach to the theory of CRP that we have recently proposed [*Phys. Rev. Lett.* **80**, 41 (1998)]. In the core of this approach lies an alternative expression for CRP in terms of the outgoing wave Green's function which is formally equivalent to the Miller's definition of this quantity in terms of the scattering matrix [*J. Chem. Phys.* **62**, 1899 (1975)] and to the Miller-Schwartz-Tromp formula [*J. Chem. Phys.* **79**, 4889 (1983)], but is direct, in contrast to the former, and more suitable for practical calculations than the latter. Furthermore, our approach rests on solid grounds of time-independent quantum scattering theory and provides an appealing competitive alternative to the absorbing potential formulation given by Seideman and Miller [*J. Chem. Phys.* **96**, 4412 (1992); **97**, 2499 (1992)]. Ideologically, it is close to the approach considered earlier for a one-dimensional model by Manolopoulos and Light [*Chem. Phys. Lett.* **216**, 18 (1993)], but is formulated from scratch for realistic systems with many degrees of freedom. The strongest point of our approach is that its final working formulas are expressed in terms of the Wigner-Eisenbud matrix, so they can be easily implemented on the basis of many existing quantum scattering codes. All these features are discussed and illustrated by calculations of the CRP and reaction eigenprobabilities for two prototypical light atom transfer reactions in heavy-light-heavy triatomic systems in three dimensions for zero total angular momentum.

I-C-4 Photo-Dynamics and Reaction Dynamics of Molecules (Satellite of ICPEC XXI)

MITSUKE, Koichiro; NAKAMURA, Hiroki

[*Comments Atom. Mol. Phys.* **2**, D75 (2000)]

The above-named satellite meeting was held in Okazaki on July 31st to August 2nd, 1999. The scientific program consisted of 21 invited lectures and 32 contributed papers covering various topics of molecular photoionization, photodissociation and chemical reaction dynamics. Several invited papers at this meeting are briefly summarized.

I-C-5 New Implementation of the Trajectory Surface Hopping Method with Use of the Zhu-Nakamura Theory

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

[*J. Chem. Phys.* **115**, 3031 (2001)]

A new implementation of the trajectory surface hopping (TSH) method is proposed to treat multi-dimensional nonadiabatic dynamics by incorporating the analytical Zhu-Nakamura semiclassical theory of nonadiabatic transition. The problem of classically forbidden hops in the TSH method can now be solved and dealt with just as easily as the classically allowed hops by introducing nonvertical hopping techniques. This is made possible, because the theory can treat both classically allowed and forbidden hops accurately in a unified way. The Zhu-Nakamura theory also enables us to predetermine important regions of potential energy surface (PES) before carrying out any dynamics calculations, and thus to save a lot of computational efforts. The charge transfer processes in the collinear H_3^+ system are studied numerically to test the new TSH method. Comparing the new and old versions of TSH with exact quantum calculations, the new method shows much better agreement with the exact calculations. It also works well when all transitions are classically forbidden and the old method fails completely.

I-C-6 Significant Improvement of the Trajectory Surface Hopping Method by the Zhu-Nakamura Theory

ZHU, Chaoyuan; KAMISAKA, Hideyuki[1]; NAKAMURA, Hiroki
([1]GUAS)

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

By taking the 3D $D^+ + H_2$ reaction system, the trajectory surface hopping method based on the Zhu-Nakamura theory is demonstrated to work much better than old one and to be very promising to treat high-dimensional electronically nonadiabatic processes. The difference between the new and old survives even at high initial vibrational states and high energies.

I-C-7 Accurate Quantum Dynamics of Electronically Nonadiabatic Chemical Reactions in the DH_2^+ System

KAMISAKA, Hideyuki[1]; BIAN, Wensheng[2]; NOBUSADA, Katsuyuki[3]; NAKAMURA, Hiroki
([1]GUAS; [2]IMS and Shandong Univ.; [3]IMS and Hokkaido Univ.)

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

Three-dimensional accurate quantum dynamics calculations are carried out for the DH_2^+ system for $J = 0$ (J: total angular momentum quantum number) by the hyperspherical coordinate approach with use of the new potential energy surfaces constructed based on the recent *ab initio* quantum chemical calculations. Not only electronically nonadiabatic reactions, *i.e.* reactive charge transfer processes, but also electronically adiabatic reactions and electronically nonadiabatic non-reactive processes are investigated. Because of the deep well on the electronically adiabatic ground surface, there appear a large number of resonances and the electronically adiabatic reactions are mostly statistical. Nonadiabatic transitions along the potential crossing seam cause deviations from the statistical behaviour and some interesting dynamical features are found.

I-D Theory of Nonadiabatic Transitions

I-D-1 Nonadiabatic Dynamics: Transitions Between Asymptotically Degenerate States

OSHEROV, Vladimir I.[1]; NAKAMURA, Hiroki
([1]IMS and Russian Acad. Sci.)

[*Phys. Rev. A* **63**, 052710 (2001)]

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

I-D-2 Nonadiabatic Transitions due to Curve Crossings: Complete Solutions of the Landau-Zener-Stueckelburg Problems and Their Applications

ZHU, Chaoyuan; TERANISHI, Yoshiaki[1]; NAKAMURA, Hiroki

(¹IMS and RIKEN)

[*Adv. Chem. Phys.* **117**, 127 (2001)]

I. Introduction
II. Physical Significance of Level Crossing
III. Complete Solutions of the Two-State Landau-Zener-Stueckelberg Problems
  A. Brief Historical Survey
  B. Complete Solutions
    1. Landau-Zener Case
    2. Nonadiabatic Tunneling Case
IV. How to Deal with Multichannel and Multidimensional Problems
  A. Multichannel Processes
    1. General Framework
    2. Numerical Applications
  B. Multidimensional Problems
V. Other Models
  A. Exponential Potential Model
  B. Rosen-Zener-Demkov Model ($\beta_1 = \beta_2 = 0$)
  C. Special Cases of Exponential Potential Model ($\beta_1 = (1/\beta_2)$)
  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
  Acknowledgments
  References

I-D-3 New Type of Nonadiabatic Dynamics: Transitions between Asymptotically Degenerate States

OSHEROV, Vladimir I.[1]; USHAKOV, Vladimir G.[1]; NAKAMURA, Hiroki
(¹IMS and Russian Acad. Sci.)

The WKB-type semiclassical analysis is carried out for a two-state model potential system, in whitch two asymptotically degenerate Morse potentials are coupled by an exponential diabatic coupling. Both crossing and non-crossing cases are treated and explicit analytical expressions for the full scattering matrix are obtained. A numerical test demonstrates the accuracy of the theory.

I-E Laser Control of Molecular Processes

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

NAGAYA, Kuninobu[1]; TERANISHI, Yoshiaki[2]; NAKAMURA, Hiroki
(¹GUAS; ²IMS and RIKEN)

[*J. Chem. Phys.* **113**, 6197 (2000)]

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 we create two nonadiabatic tunneling (NT) type curve crossings between the ground electronic bound state shifted up by one photon energy 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-E-2 New Way of Controlling Molecular Processes by Lasers

TERANISHI, Yoshiaki[1]; NAGAYA, Kuninobu[2]; NAKAMURA, Hiroki
(¹IMS and RIKEN; ²GUAS)

[*Adv. in Multi-Photon Processes and Spectroscopy* **14**, R. J. Gordon and Y. Fujimura, Eds., World Scientific, pp. 215–227 (2000)]

Two new ways of controlling molecular processes are proposed. One is to weep laser frequency and/or intensity at avoided crossings among dressed states to control nonadiabatic transitions there. The second is to use the intriguing phenomenon of complete reflection in the nonadiabatic tunneling type transition in the time-independent framework. The newly completed semiclassical theory of nonadiabatic transitions can give a nice analytical formulation for these.

I-E-3 Selective Excitation Among Closely Lying Multi-Levels

NAGAYA, Kuninobu[1]; TERANISHI, Yoshiaki[2]; NAKAMURA, Hiroki
([1]GUAS; [2]IMS and RIKEN)

[*Laser Control and Manipulation of Molecules*, Amer. Chem. Soc., in press]

A new idea is proposed to accomplish selective and complete excitation to any specified state among closely lying multilevels. The basic idea is to control nonadiabatic transitions among dressed states by sweeping the laser frequency periodically. Both three- and four-level models are treated by the semiclassical theory of nonadiabatic transition and conditions of complete excitation are formulated. Numerical demonstrations are presented in comparison with the π-pulse and adiabatic rapid passage.

I-E-4 Control of Molecular Processes by a Train of Linearly Chirped Pulses: Selective and Complete Excitation

NAGAYA, Kuninobu[1]; TERANISHI, Yoshiaki[2]; NAKAMURA, Hiroki
([1]GUAS; [2]IMS and RIEKN)

A new scheme of controlling molecular processes is proposed. The scheme is to manipulate nonadiabatic transitions among Floquet states and can be formulated analytically. Complete selective excitation among closely lying levels and complete electronic excitation of a diatomic molecule are numerically demonstrated. This is proved to be better and more robust compared to the other methods such as the phase-lock and the adiabatic rapid passage. Experimental realizability can also be expected, since linear chirping can be now relatively easily manipulated.

I-F Theory of Multi-Dimensional Tunneling

I-F-1 Practical Implementation of the Instanton Theory for the Ground State Tunneling Splitting

MIL’NIKOV, Gennady V.[1]; NAKAMURA, Hiroki
([1]IMS and Inst. Struct. Macrokinetics)

[*J. Chem. Phys.* **115**, 6881 (2001)]

The instanton theory is reformulated with use of the path integral approach and the WKB approximation to the Schrödinger equation. Both approaches are shown to provide the same results. A new practically useful semiclassical formula is derived for the tunneling splitting of the ground state, which can be implemented for high-dimensional systems. The theory is applicable to systems of arbitrary Riemannian metric and is also supplemented by a practical numerical recipe to evaluate the instanton trajectory, *i.e.* periodic orbit, in multidimensional space. Numerical examples are presented for 3D and 21D systems of HO_2 and malonaldehyde, respectively.

I-G New Methods for Scattering Calculation

I-G-1 Stable and Efficient Evaluation of Green’s Function in Scattering Problem

MIL’NIKOV, Gennady V.[1]; NAKAMURA, Hiroki; HORÁČEK, Jiri[2]
([1]IMS and Inst. Struct. Macrokinetics; [2]IMS and Charles Univ. Prague)

[*Comput. Phys. Commun.* **135**, 278 (2001)]

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-G-2 Use of Diabatic Basis in the Adiabatic-By-Sector R-Matrix Propagation Method in Time-Independent Reactive Scattering Calculations

MIL’NIKOV, Gennady V.[1]; NAKAMURA, Hiroki
([1]IMS and Inst. of Struct. Macrokinetics)

[*Comput. Phys. Commun.* **140**, 381 (2001)]

We propose a new recipe for the *R*-matrix propagation which combines the ideas of the adiabatic-by-sector (ABS) method and the sequential diagonalization/truncation technique. The *R*-matrix is determined in the adiabatic representation but the method does not require calculations of adiabatic channel functions at radial points inside the sector of propagation. This is a modification of the previously proposed ABS approach and can significantly reduce the computational time and memory in the energy independent part of scattering calculations. The code is checked by a test calculation of the reaction $O(^3P) + HCl \rightarrow OH + Cl$ 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-3 Regularization of Scattering Calculations at R-Matrix Poles

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

Physical quantities of scattering expressed in terms of R-matrix are not well defined at *R*-matrix poles. It is shown that these unphysical singularities can be removed and the regularized expressions are obtained. The method is straightforwardly applicable to various quantities of scattering theory such as reactance matrix, Green's functions, cumulative reaction probability and density of resonance states.

I-H Theoretical Study of Dissociative Attachment

I-H-1 Study of Dissociative Electron Attachment to HI Molecule by Using R-Matrix Representation for Green's Function

KOLORENČ, P.[1]; HORÁČEK, Jiri[2]; MIL'NIKOV, Gennady V.[3]; NAKAMURA, Hiroki
([1]Charles Univ. Prague; [2]IMS and Charles Univ. Prague; [3]IMS and Inst. Struct. Macrokinetics)

The new method of the calculation of scattering Green's function recently proposed by the authors is applied to the process of dessociative attachment of low-energy electrons to HI molecule previously considered by Horáček, Domcke and Nakamura. The calculation is extended to vibrationally and rotationally excited target gas molecules. The temperature dependence of the dissociative attachment cross section is studied in details.

I-I 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 dynamic 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-I-1 Two-Dimensional Spectroscopy and the Harmonically Coupled Anharmonic Oscillators

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

[*Chem. Phys.* **266**, 237 (2001)]

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-I-2 Two-Dimensional Raman and Infrared Signals Measured from Different Phase-Matching Conditions

KATO, Tsuyoshi; TANIMURA, Yoshitaka

[*Chem. Phys. Lett.* **341**, 329 (2001)]

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 achieved experimentally.

I-I-3 Nonequilibrium Initial Conditions of a Brownian Oscillator System Observed by Two-Dimensional Spectroscopy

SUZUKI, Yoko; TANIMURA, Yoshitaka

[*J. Chem. Phys.* **115**, 2267 (2001)]

We study effects of a nonequilibrium initial condition of a Brownian oscillator system upon two-, three-, and four-time correlation functions of an oscillator coordinate as a subject of multi-dimensional spectroscopy. A nonequilibrium initial condition is set by a displacement of a Gaussian wave packet in an oscillator potential. Such situation may be found in a vibrational motion of molecules after a sudden bond breaking between a fragmental molecule and a targeting vibrational system or a movement of wave packet in an electronic excited state potential surface created by a laser pump pulse. Multi-time correlation functions of oscillator coordinate for a nonequilibrium initial condition are calculated analytically with the use of generating functional from a path integral approach. Two-, three- and four-time correlation functions of oscillator coordinates correspond to the third-, fifth-, and seventh-order Raman signals or the first-, second-, and third order infrared signals. We plotted these correlation functions as a signal in multi-dimensional spectroscopy. The profile of the signal depends on the initial position and momentum of the wave packet in the fifth- and seventh-order Raman or the second and third order infrared measurement, which makes it possible to measure the dynamics of the wave packet directly in the phase space by optical means.

I-I-4 Higher-Order Vibrational Correlation Functions of a Single Harmonic Oscillator Nonlinearly Coupled with a Thermal Bath I: Gauss-White Noise Case

KATO, Tsuyoshi; TANIMURA, Yoshitaka

Higher-order vibrational correlation functions of a single harmonic oscillator system nonlinearly coupled with harmonic oscillators bath are studied in relation to the 2D Raman or IR spectroscopy. The nonlinear system-bath coupling models the vibrational relaxation dynamics under the presence of the elastic and inelastic relaxation mechanisms. A quantum Fokker-Planck equation is derived to describe the relaxation processes for the Gaussian-white noise. Effects of the simultaneous existence of two relaxation mechanisms, the system-bath coupling strength and the temperature are investigated and compared with the Brownian oscillator model by numerically integrating the Fokker-Planck equation. We observe new optical responses induced by the coexistence of the two relaxation mechanisms, which can possibly be very pronounced in the fifth-order Raman (or second-order IR) spectroscopy rather than the seventh-order Raman (or third-order IR) spectroscopy.

I-I-5 Higher-Order Vibrational Correlation Functions of a Single Harmonic Oscillator Nonlinearly Coupled with a Thermal Bath II: Gauss-Markov Noise Case

KATO, Tsuyoshi; TANIMURA, Yoshitaka

A single harmonic oscillator system nonlinearly coupled to harmonic oscillators bath is considered to study the effects of the finiteness of the Gaussian-Markovian bath correlation time. The previously derived quantum Fokker-Planck equation is extended in a hierarchy form to treat arbitrary bath correlation time. The equation describes the vibrational frequency fluctuations as well as the vibrational energy relaxation processes, and can treat strong system-bath couplings. The fifth- and seventh-order Raman response functions are calculated by numerically integrating the Fokker-Planck equation for various system-bath coupling strengths and bath correlation times. Echo behaviors can be observed in the seventh-order Raman response under the slow frequency fluctuation and energy relaxation, however, such the behavior is absent in the leading fifth-order response function. This finding cannot be predicted by the available stochastic Gaussian frequency fluctuation model.

I-I-6 Two-Dimensional Spectroscopy for a Two-Dimensional Rotator in a Dissipative Environment

SUZUKI, Yoko; TANIMURA, Yoshitaka

Effects of an environment on the dynamics are more clearly characterized by the multidimensional spectroscopy than one-dimensional spectroscopy measured in the microwave absorption. We investigate the two-dimensional spectroscopy of a two-dimensional quantal rotator coupled to a Gaussian-Markovian harmonic oscillator bath by calculating a four-time correlation function of a dipole whose analytical form is derived from the generating functional. Such spectra are experimentally proved by the third order absorption. The spectra in the absence of damping are discrete and reveal transitions between eigenstates of the angular momentum quantized due to the cyclic boundary condition. The calculations for a damped rotator predict an echo signal that can be understood by the Liouville space path ways. The profile of the two-dimensional spectroscopy depends on a finite correlation time of the bath fluctuation and of a coupling strength.

I-I-7 Two-Dimensional Spectroscopy for Molecular Vibration: An Analysis of Potential Surfaces in a Dissipative Environment

MARUYAMA, Yutaka; TANIMURA, Yoshitaka

A molecular vibrational mode in condensed phases is studied using a quantum Fokker-Planck equation, which can treat a molecular system with any shape of potential coupled to a white noise heat-bath. The two-, three-, and four-time correlation functions of Raman polarizability and the dipole moment are calculated as the subject of two-dimensional (2D) spectroscopy for various potential surfaces with different heat-bath coupling strength. The temporally 2D profiles of signal are very sensitive to the potential surfaces and a coordinate dependence of the polarizability or dipole even in the strong damping case. This indicates that 2D spectroscopy allows us to access information of the potential and the polarizability or dipole in the dissipative environment, where the line shape of conventional 1D Raman or infrared spectroscopy is broadened and does not provide such information.

I-J The Condensed Phase Quantum Dynamics of Molecules and Atoms

We investigate quantum dynamics of molecules or atom in 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-J-1 Quantum Theory of Two-Dimensional Rotator in a Dissipative Environment: Application to Infrared Spectroscopy

SUZUKI, Yoko; TANIMURA, Yoshitaka

[*J. Phys. Soc. Jpn.* **70**, 1167 (2001)]

Quantum coherence and its destruction by coupling to a dissipative environment play important roles in time-resolved optical response. We study a two-time correlation function of a two-dimensional rotator coupled to a harmonic-oscillator bath. Generating functionals of reduced density matrix elements for the rotator degrees of freedom are calculated by diagonalizing the total Hamiltonian with the use of unitary transformations and then performing path integrals. A closed-form expression of linear absorption spectrum for a dipole rotator, *i.e.*, a Fourier transformation of the dipole two-time correlation function, is derived from the generating functionals characterized by the bath spectral density. Based on the theory, the spectra for a methyl rotation in a toluene are depicted for various damping constants and temperatures. Because of the cyclic boundary condition that is constrained to fit the rotator degree of freedom, the energy states of the rotator in the absence of damping are discrete: the spectra consist of rotational branches, which correspond to change of the angular momentum. Owing to damping, the spectra exhibit a continuous band which is broadened as temperatures increase.

I-J-2 Two Time Correlation Function of a Two-Dimensional Quantal Rotator in a Colored Noise

SUZUKI, Yoko; TANIMURA, Yoshitaka

We study an absorption spectrum of a two-dimensional rotator coupled to a harmonic Gaussian-Markoffian heat bath. Generating functional of reduced density matrix elements for the rotator degrees of freedom in the Gaussian-White case have been developed and are presented compactly in the recent letter. We extend it to the Gaussian-Markoffian case and show the detailed calculation in this paper. A linear absorption spectrum for a dipole rotator is analytically derived from the generating functional. Representative calculations for a methyl rotator in a toluene of the spectra are presented with the use of the analytical result. Plots for various damping strength, cutoff frequency, and temperatures take into account the environmental effect to the dynamical properties of the dipole moment.

I-J-3 Coherent Control of Nonclassical Effects in Quantum Optical Three-Level Atomic System

DU, Si-de; TANIMURA, Yoshitaka

Nonclassical effects are theoretically investigated in the interaction of a single three-level atom with a single one-mode quantized cavity field. The atom under consideration has two closely spaced excited levels and one ground-state level. When the atom is coherently excited into a superposition of the two excited states, there exists quantum interference between two transition channels which are stimulated by the cavity field initially in coherent states. We have discussed influence of quantum interference on collapses and revivals, squeezing and antibunching. It is discovered that the revival patterns strongly depend on quantum interference, and quantum interference can produce strong squeezing and antibunching. Our results are useful for understanding and controlling nonclassical effects.

I-K Theoretical Studies of Correlated Electron Systems

We study biorthogonal formulation of correlated electron system represented in the second quantized form. We illustrate the transcorrelated Hamiltonian approach and discuss the self-consistent field theory using biorthogonal orbitals.

I-K-1 Biorthogonal Approach for Explicitly Correlated Calculations Using the Transcorrelated Hamiltonian

HINO, Osamu; TEN-NO, Seiichiro[1]; TANIMURA, Yoshitaka
([1]Nagoya Univ.)

A biorthogonal formulation is applied to the nonhermite transcorrelated Hamiltonian, which treats a large amount of the dynamic correlation effects implicitly. We introduce biorthognal canonical orbitals diagonalizing the nonhermite Fock operator. We also formulate many-body perturbation theory for the transcorrelated Hamiltonian. The biorthogonal self-consistent fields followed by the second order perturbation theory are applied to some pilot calculations including small atoms and molecules. We illustrate the transcorrelated Hamiltonian approach and discuss the self-consistent field theory using biorthogonal orbitals. We develop MBPT for the transcorrelated Hamiltonian based on the biorthogonal formalism. We also explain the approximate calculations of three-electron integrals, which appear in the transcorrelated method.

I-L 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. Furthermore, the analysis of genome sequences from various species including human have been performed quite rapidly. The next significant problem is to clarify 3D structures and functions of proteins coded by genome sequences. Since the experimental techniques to determine 3D structures of proteins are still time-consuming, a predictive technique is desired. However, a prediction of protein 3D strcutures is still unsolved and difficult problem in the area of molecular biophysics. Currently, we are attempting to predict location of 3D strcuture units, so-called domains, in genome sequences by means of a kind of contact map based on the statistics of average distances between amino acids in proteins. This information can be helpful to determine the 3D structure of each structural unit. 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 applied a 3D search method to find a new potent inhibitor of an enzyme for development of a new herbicide. We also made the MD simulation of some polysacchalydes, chitosan and amylose, to clarify the relationship between their dynamical properties and the coloring bahavior with iodine.

I-L-1 Contact Maps Derived from the Statistics of Average Distances between Residues in Proteins. Application to the Prediction to the Prediction of Structiures and Active-Sites of Protein and Peptides

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

[*Recent Res. Dev. Protein Eng.* in press]

Information on various 3D structural features of proteins is extractable from statistics of protein 3D stuctures, using the method we review here. The main tool for the method is a contact map, called an average diatance map (ADM), constructuted from the statistics of average distances between residues. In spite of their simplicity, theese maps proveide various predictions on 3D structures of proteins, *e.g.*, location of domains, structural similarity between proteins, proteins structural classes, active sites in bioactive peptides, and so on. The present method is useful for practical problems encountered in protein engineering and drug design. We also demonstrate a practical application of the present method to the structure-activity relationship prediction of an insect peptidic hormone; the results have ramifications for the future development of new types of insecticides. Further, ADM can be applied for identification of functional units on genome sequences in the post-genome era.

I-L-2 Prediction of Protein 3D Folding Properties in Genome Sequences Based on the Statistics of Average Distances between Residues

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

[*4th International Conference on Biological Physics* L33 (2001)]

The analyses of human genome has been proceeded quite rapidly and whole human genome will be uncovered in very near future. The next significant step is to predict the 3D structure and function of domains in an Open Reading Frame (ORF) derived from a genome analysis, *i.e.* to clarify which region in an ORF corresponds to what kind of functional domain. The average distance (ADM) method is useful and adequate for the step of prediction of domain locations on ORFs. The ADM method also gives several predictions on 3D structures of proteins. In the present work, we report the recent progress of the ADM method to treat ORFs derived from genome analyzes especially focusing on the prediction of location and folding properties of domains. The results show that the ADM method predicts folding units in a protein sequence and it corresponds to a functional domain in many cases.

I-L-3 Identification of Novel Potent Inhivitors for ATP-Phosphoribosyl Transferase Using Three-Dimensional Structural Database Search Technique

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[*QSAR* **20**, 143 (2001)]

An efficient method to search potent inhibitors of an enzyme or a receptor is required in the process of drug design. One simple but effective strategy is to search compounds fit to the cavity of a receptor from the compound 3D database. We identified new potent inhibitors for ATP-phosphoribosyl transferase, which acts at the first step of histidine biosynthesis pathway, using a 3D database search technique. The 3D search was based on the structure of the product molecule, N-1-(5'-phosphoribosyl-1-pyrophosphate), *i.e.* bi-substrate mimicking. Four compounds with three different chemical classes were examined. Among them, amino-(chlorophenyl)-triazolopyrimidine compounds, which are the simplest and smallest ones, showed potent activity. The structural comparison with the product molecule suggests that the simultaneous occupation of two substrate-binding sites likely enhances the enzyme inhibition. The most potent compound examined in this study was a disulfide-bond containing molecule, whose mode of action seems to be different from others.

I-L-4 Complex Formation of Chitosan with Iodine and Its Structure and Spectroscopic Properties—Molecular Assembly and Thermal Hysteresis Behavior

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[*Int. J. Thermodyn.* **22**, 1265 (2001)]

To elucidate the factors responsible for the complexation of chitosan with iodine and to gain insight into the structures and spectroscopic properties of chitosan-iodine (CI) complexes, extensive studies were performed on the effects of iodine/chitosan concentrations and temperature on the CI complexation. That is, the several physicochemical properties of the complex in acidic solutions containing excess KI were examined by means of various spectroscopic (absorption, CD, *etc.*) and structural analyses (SAXS, *etc.*) and molecular dynamics (MD) simulations. The CI complex exhibited absorption spectra with a peak at around 500 nm, regardless of the iodine/chitosan concentrations and temperature. Correspondingly, the CI complexes exhibited mutually split CD bands with opposite signs (+, –) at around 500 nm. The CI complex showed thermal hysteresis, *i.e.*, an irreversible reaction process involved in complexation and color formation. MD calculations predicted that the irreversibility and thermal hysteresis behavior of the CI complexes are due to a crystalline-like extended compact folded conformational transition.

I-M Electronic Properties of Nanostructured Materials

I-M-1 Electronic Structure of K-Doped Carbon Nanotubes

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([1]Tokyo Inst. Tech.; [2]IMS and Tokyo Inst. Tech.)

[submitted]

Alkali-metal doping is expected to provide a means of controlling electronic properties of carbon nanotubes. Previous band structure calculations support the charge-transfer picture in both K and Li doping. However, more systematic analysis is desirable, since transport properties of nanotubes are sensitive to their size and chirality. We study the effect of K doping inside a few zigzag nanotubes by using density functional method. We find that the effect depends on the diameter significantly, and it is not described fully by the simple charge-transfer picture. In particular, in the (10,0) and (12,0) tube, which are possible to produce macroscopic amount, the nearly free electron (NFE) state of the nanotube is pulled down by hybridization with the K 4s state, and crosses the Fermi level. We will discuss the influence on transport properties from the spatial distribution of the NFE state.

I-M-2 Geometries, Electronic Properties, and Energetics of Isolated Single Walled Carbon Nanotubes

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([1]Tokyo Inst. Tech.; [2]IMS and Tokyo Inst. Tech.)

[submitted]

Using the density-functional electronic-structure calculations, we study so-called zig-zag carbon nanotubes. From the complete geometry optimization, it is found that two kinds of bond lengths are considerably different from each other. They possess strong tube-diameter dependence. In addition, changes of the electronic band structure upon the geometry relaxation from the uniform bond-length tube are found to be sizable. Also the electronic properties and energetics obtained are discussed in detail.

I-N 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, surface-induced phase transition phenomena, and entropic excluded-volume effects in colloidal and biological systems.

I-N-1 Long-range Interaction between Hydrophilic Surfaces Immersed in a Hydrophobic Fluid Containing a Hydrophilic Component at Low Concentration

KINOSHITA, Masahiro
(Kyoto Univ. and IMS)

[*Chem. Phys. Lett.* **333**, 217 (2001)]

Behavior of a hydrophobic fluid containing a hydrophilic component at low concentration, which is confined between macroparticles separated by distance *L*, is analyzed using the RISM-HNC theory. When the hydrophilicity of the macroparticle surface is sufficiently high, the following is observed. A layer within which particles of the hydrophilic component are enriched is formed around each macroparticle. As *L* decreases the two enriched layers within the confined domain continue to grow, eventually leading to a phase transition. The range of the macroparticle interaction induced can be far longer than the molecular scale.

I-N-2 Statistical-Mechanical Analysis on Entropically Driven Formation of Ordered Structure

KAMIO, Kazunori[2]; KINOSHITA, Masahiro[1]
([1]Kyoto Univ. and IMS; [2]Kyoto Univ.)

[*Kagaku Kogaku Ronbunshu* (in Japanese) in press]

Phase separation in a mixture of small and large colloidal particles and the interaction induced between a macromolecule (a large particle) and a cell membrane (a surface) immersed in smaller molecules (small particles), have been analyzed using an integral equation theory. Simplified models are employed to study the entropically driven formation of ordered structure, which is ascribed to the excluded volume effects (forces of increasing the system entropy by reduction of the total excluded volume for the small particles). In the analysis on the induced interaction, attention is focused on effects due to the packing fraction of the small particles, the diameter of the large particle, the surface curvature, presence of a small amount of particles slightly larger than the small particles, and attractive interaction between the small particles. A significant result is that great specificity is provided between the diameter of the large particle and the surface curvature. Works concerning the roles of the excluded volume effects on the "lock and key" steric interactions between macromolecules and protein folding in the biological systems, which are in progress in our group, have also been discussed.

I-N-3 Depletion Effects on the Lock and Key Steric Interactions between Macromolecules

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

The hypernetted-chain (HNC) equations solved on a three-dimensional cubic grid are employed to calculate the spatial distribution of the depletion potential between a big solute of *arbitrary geometry* and a big sphere immersed in small spheres forming the solvent. Effects of the step edge on the lateral depletion force along a wall surface are analyzed and shown to be in qualitatively good agreement with a recent experimental observation. Simple model calculations are performed for the *lock and key* steric interactions between macromolecules, and it is found that the depletion effects provide the interactions with remarkably high selectivity.

I-N-4 Improvement of the Reference Interaction Site Model Theory for Calculating the Partial Molar Volume of Amino Acids and Polypeptides

KINOSHITA, Masahiro[1]; IMAI, Takashi; KOVALENKO, Andriy; HIRATA, Fumio
([1]Kyoto Univ. and IMS)

[*Chem. Phys. Lett.* **348**, 337 (2001)]

We propose a simple, efficient bridge correction of the one-dimensional reference interaction site model (RISM) theory. By combining the modified RISM method with the Kirkwood-Buff theory, the partial molar volume is calculated for the 20 amino acids and for oligopeptides of glutamic acids in extended and a-helix conformations. The bridge correction drastically improves agreement between the calculated values and the experimental data.

I-N-5 Spatial Distribution of Depletion Potential between a Big Solute of Arbitrary Geometry and a Big Sphere Immersed in Small Spheres

KINOSHITA, Masahiro
(Kyoto Univ. and IMS)

[*J. Chem. Phys.* submitted]

The hypernetted-chain integral equations are solved on a three-dimensional cubic grid to calculate the spatial distribution of the depletion potential between a big solute of *arbitrary geometry* and a big sphere immersed in small spheres forming the solvent. By analyzing the potential along a specific trajectory of the big sphere, effects due to the geometric feature of the big solute (step edges, trenches, corners, changing curvature, *etc.*) can be examined in detail. As an illustration, effects of the step edge on the lateral depletion potential along a wall surface are analyzed. Along the trajectory considered, the big sphere moves at constant height, starting on the center of the wall surface and moving horizontally past the edge. The potential minimum occurs not on the center but at a location much closer to the edge. The big sphere is repelled from the edge into the wall surface, and to escape to the bulk it must overcome a significantly high free-energy barrier. A positive peak of the potential occurs near the edge on the bulk side. As another illustration, simple model calculations are performed for the *lock and key* steric interaction between macromolecules. The potential at contact (*i.e.*, the stabilization free energy) for the key that exactly fits the lock is far larger than for smaller and larger keys and considerably in excess of the value predicted by the Asakura-Oosawa (AO) theory. A very high free-energy barrier features the potential for a smaller key, preventing its access to the lock. The depletion effects on the interaction are substantially large, and the selectively given is remarkably high. The physical origin of the failure of the AO theory is discussed in detail.

I-O Electronic Structures of Polymers and Organic Molecular Crystals

In order to understand the electronic, optical, and magnetic properties of polymers and organic molecular crystals, we have investigated the electronic structures of these materials using various kinds of theoretical approaches, for examples, the density matrix renormalization group method for a model Hamiltonian, a first-principles pseudopotential method, and ab initio quantum chemical calculations. In particular, we have focused our attention mainly to phase transition phenomena accompanied by drastic changes of electronic and optical functions. The actual targets of our research are as follows: 1) Semiconductor-metal transition in doped conducting conjugated polymers, 2) Thermo- and photochromic phase transitions in polydiacetylene, 3) Neutral-ionic transition in tetrathiafulvalene-p-chloranil.

I-O-1 Charge Carriers and Semiconductor-Metal Transition in Doped Conducting Conjugated Polymers

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We have investigated how the configurations of charge carriers evolve in non-degenerated conjugated polymers when carrier concentration increases, putting emphasis on electron correlation effects and electron-lattice coupling. For this purpose, we have applied the density matrix renormalization group method to the one-dimensional extended Hubbard-Peierls model. We found out theoretically a new configuration of charge carrier, polaron-pair state, as an intermediate configuration between polaron and bipolaron. This configuration is possible under a relatively weak electron-lattice coupling. We have shown that gaps for charge and spin excitations become quite small at highly doping concentration. Comparing the non-interacting case, correlation effects suppress the gap, indicating the significant role of electron-electron interaction on semiconductor-metal transition of which mechanism is still open question.

I-O-2 First-Principles Study of Polydiacetylene

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In order to elucidate the mechanism of thermo- and photochromic phase transitions in polydiacetylene (PDA), we have performed first-principles pseudopotential calculations for a typical theromochromic PDA, TCDU, (poly(5,7-dodecadiyne-1,12-diyl-bis-phenylurethane)). The calculated energy surface shows that the butatrinene conformation of backbone chain is not a metastable state in TCDU, in contrast to a hypotetical PDA where the side group is replaced by a hydrogen atom. This indicates that the side group has significant influence on the geometry of the backbone, consistent with experimental observations. We have investigated how the conformation of side group affects the energy surface and band gap in order to understand the interplay between the π-electronic structure at backbone and the configuration of side group more clearly.

I-O-3 Role of Intramolecular Charge Distribution on Neutral-Ionic Transition of Tetrathiafulvalene-*p*-Chloranil

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[*Phys. Rev. B* **64**, 205107 (2001)]

We calculated the Madelung energies of both the ground state and excited states in tetrathiafulvalene-*p*-chloranil (TTF-CA) by taking into account intramolecular charge distribution. The distribution is found to be significant in the neutral-ionic (NI) transition. In the ionic phase, the Madelung energy depends more strongly on the intermolecular distance perpendicular to the π-stacking chains than on that along the chains. This indicates that simple single-chain models neglecting interchain electrostatic coupling are not adequate. The gain of the Madelung energy due to dimerization is concluded to be small compared with the other structural changes. We also calculated the formation energy of excited state domains, which appear in the initial process of the phase transition. A one-dimensional excited domain has the smallest energy among the possible domains with the same number of molecules, and the energy per molecule is considerably reduced in increasing the domain size. It is consistent with the experimental suggestion that a large number of excitations were generated by only one photon.

I-P 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;

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

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-P-1 Theoretical Study on the Structures and Energies of Acetic Acid Dimers in Aqueous Solution

NAKABAYASHI, Takakazu; SATO, Hirofumi; HIRATA, Fumio; NISHI, Nobuyuki

[*J. Phys. Chem. A* **105**, 245 (2001)]

The effects of hydration on the dimerization energies and structures of acetic acid dimers are studied by the reference interaction site model self-consistent-field (RISM-SCF) method. Comparisons of the RISM-SCF results are also made with those obtained from the self-consistent reaction field (SCRF) methods to examine the dielectric effects of the solvent. The RISM-SCF method predicts the marked stabilization due to solvation in the dimer structures with large dipole moments. From the decomposition analysis of the excess chemical potential, the contribution from the free carbonyl oxygen is found to be much larger than the other atoms for the stabilization of these dimers in aqueous solution. Such a stabilization in the polar dimers is not obtained from the simplest SCRF method that considers only the solute dipole.

I-P-2 Realization of Three-Dimensional Solvation Structures from the Site-Site Radial Distribution Functions in Liquids

SATO, Hirofumi; HIRATA, Fumio

[*Bull. Chem. Soc. Jpn.* **74**, 1831 (2001)]

We propose a new procedure to realize a three-dimensional (3D) solvation structure around a solute molecule from a set of radial distribution functions (RDF), or distance information. The method consists of the minimization of a penalty function defined as the mean-square difference of the solute-solvent interatomic distances obtained from trial 3D configurations and from target RDFs. The hydration structures around several different solute molecules are visualized to demonstrate the method.

The solvation structures realized with the present method correspond to the most plausible solvation structure (MPSS), which looks like a “snap shot” of the molecular dynamics trajectory. However, the MPSS is essentially different from the “snap shot,” since it represents an average configuration, and is therefore an observable quantity. The present procedure was originally developed for analyses of the RDF results obtained from the reference interaction site model (RISM), but can be applied straightforwardly to RDFs from other sources, such as molecular simulations and scattering experiments.

I-P-3 Solvent Effect on the Nuclear Magnetic Shielding: Ab initio Study by the Combined Reference Interaction Site Model and Electronic Structure Theories

YAMAZAKI, Takeshi[1]; SATO, Hirofumi; HIRATA, Fumio
([1]GUAS)

[*J. Chem. Phys.* **115**, 8949 (2001)]

A method for calculating the nuclear magnetic shielding constant of atoms in solution is proposed based on the *ab initio* electronic structure theory combined with the extended reference interaction site model in statistical mechanics for molecular liquids. The method is applied to a water molecule solvated in water, acetone, chloroform, and carbon tetrachloride. The results for solvation effect demonstrate capability to predict the experimental results. The theory provides a tool to investigate the solvent effect on the nuclear magnetic shielding and its temperature dependence from a molecular view point. The theory takes account for effect of the electrostatic interaction on the electronic structure of solute, but disregards the electron overlap. The effect of intermolecular overlap of electron on the nuclear magnetic shieldings is examined using a molecular cluster model.

I-Q 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-Q-1 Hydration Structure and Stability of Met-Enkephalin Studied by a Three-Dimensional Reference Interaction Site Model with a Repulsive Bridge Correction and a Thermodynamic Perturbation Method

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[*J. Chem. Phys.* **113**, 9830 (2000)]

We study the hydration structure and free energy of several conformations of Met-enkephalin in ambient water by employing the one-dimensional (1D) as well as three-dimensional (3D) reference interaction site model (RISM) integral equation theories, complemented by the hypernetted chain (HNC) closure with the repulsive bridge correction (RBC). The RBC contribution to the excess chemical potential of solvation is calculated by means of the thermodynamic perturbation theory (TPT), which crucially reduces computational burden and thus is especially important for a hybrid algorithm of the RISM with molecular simulation. The 3D-

RISM/HNC+RBC-TPT approach provides improved prediction of the solvation thermodynamics and gives a detailed description of the solvation structure of a biomolecule.

The results obtained are discussed and compared to those following from the 1D-RISM/HNC theory. The latter yields physically reasonable results for the conformational stability of biomolecules in solution, which is further improved by adding the 1D-RBC. The modified, 1D-RISM/HNC-RBC-TPT integral equation theory combined with the simulated annealing or generalized-ensemble Monte-Carlo simulation methods is capable of reliable prediction of conformations of biomolecules in solution with due account for the solvent effect at the microscopic level.

I-Q-2 Theoretical Study for Partial Molar Volume of Amino Acids and Poly-Peptides by the Three-Dimensional Reference Interaction Site Model

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[*J. Chem. Phys.* **114**, 9506 (2001)]

We calculate the partial molar volume (PMV) of twenty amino acids in aqueous solution at infinite dilution is by using the Kirkwood-Buff equation and the three-dimensional reference interaction site model (3D-RISM) integral equation theory for molecular liquids. As compared to the conventional, one-dimensional (1D-RISM) approach, the results exhibit drastic improvement for the quantitative agreement with experiment. The deviation from the experimental data, seen for the relatively large amino acids is discussed in terms of the "ideal fluctuation volume" introduced in the previous study based on the 1D-RISM to account for flexibility of solute molecules. Robustness of the new approach is further demonstrated by applying it to the PMV of poly-glutamic acids in aquous solution. The method provides reasonable account for the PMV increase with the chain length, both in a-helical and extended structures, whereas the 1D-RISM approach gives an unnatural decrease of the PMV for the a-helix with a complete turn of the backbone.

I-Q-3 Theoretical Study for Volume Changes Associated with the Helix-Coil Transition of Polypeptides

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[*Biopolymers* **59**, 512 (2001)]

We calculate the partial molar volumes and their changes associated with the coil(extended)-to-helix transition of two types of peptide, glycine-oligomer and glutamic acid-oligomer, in aqueous solutions by using the Kirkwood-Buff solution theory coupled with the three-dimensional reference interaction site model (3D-RISM) theory. The volume changes associated with the transition are small and positive. The volume is analyzed by decomposing it into five contributions following the procedure proposed by Chalikian and Breslauer: the ideal volume, the van der Waals volume, the void volume, the thermal volume, and the interaction volume. The ideal volumes and the van der Waals volumes do not change appreciably upon the transition. In the both cases of glycine-peptide and glutamic acid-peptide, the changes in the void volumes are positive, while those in the thermal volumes are negative, and tend to balance those in the void volumes. The change in the interaction volume of glycine-peptide does not significantly contribute, while that of glutamic acid-peptide makes negative contribution.

I-R 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.

References
1) F. Hirata, *J. Chem. Phys.* **96**, 4619 (1992).
2) S. Chong and F. Hirata, *Phys. Rev. E* **57**, 1691 (1998).
3) S. Chong and F. Hirata, *J. Chem. Phys.* **108**, 7339 (1998).

I-R-1 Site-Site Mode-Coupling Theory for the Shear Viscosity of Molecular Liquids

YAMAGUCHI, Tsuyoshi; HIRATA, Fumio

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

A mode-coupling expression for the shear viscosity coefficient of dense molecular liquids based on the interaction site model is presented. It is a natural extension of the corresponding theory for simple liquids, in which the shear stress auto correlation function is described as the linear combination of the bilinear products of the site-site dynamic structure factor. The theory is applied to water at the ambient condition. The agreement between the theory and the computer experiment is fairly good for the simplicity of the theory.

I-R-2 Solute-Shape Dependence in Solvation Dynamics: Investigated by RISM Theory

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OKADA, Tadashi[1]
([1]Osaka Univ.)

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

A combination of the reference interaction-site model (RISM) theory and the site-site Smoluchowski-Vlasov equation has been applied to estimate solute-shape dependence of the dynamic average-energy relaxation of the solute-solvent system in a polar solvent. If the solute became larger, like octapoles, the relaxation got much slower. A plausible mechanism of the relaxation will be discussed.

I-R-3 Nonlinear Response of Solvent Molecules Induced by Instantaneous Change of Solute Electronic Structure: Studied by RISM Theory

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[*J. Mol. Struct.* **565–566**, 31(2001)]

We have applied the reference interaction-site model (RISM) theory for the estimation of the dynamic response function of the average-energy relaxation, $S_S(t)$, of the solute-solvent systems, induced by an instantaneous change of the solute electronic structure in polar solvents. We choose the solutes including square- or cubic-like structures: initially all the atoms are electrically neutral and, then we put δ^+ and δ^- charges instantaneously. For the multipoles $S_S(t)$s show apparent dependence on *d*, which predicts nonlinear response of the solvent, because $S_S(t)$ is a normalized quantity irrespective of δ as far as the linear response of the solvent dynamics is assumed. On the other hand we have previously performed transient hole-burning and time-resolved fluorescence spectroscopy. We have found the difference between the dynamic response functions obtained from spectral widths and that from spectral peak shifts, implying the nonlinear solvent-response, as these two kinds of the response functions should again correspond to each other within a linear response regime. Our present results from the RISM theory can be another indicative to confirm nonlinearity suggested by our experiments. At the moment we ascribe the origin of the nonlinear solvent behavior to the larger local-density fluctuation around the solute.

I-R-4 Average Energy Relaxation and Rearrangement of Solute-Solvent Radial Distribution Function in Solvation Dynamics: A Connection between Spectroscopic Results and RISM Theory

NISHIYAMA, Katsura[1]; HIRATA, Fumio;
OKADA, Tadashi[1]
([1]Osaka Univ.)

[*J. Mol. Liq.* **90**, 251(2001)]

We calculate the relaxation dynamics of the average energy of solute-solvent systems as well as time-dependent solute-solvent radial distribution functions by means of the reference interaction-site model (RISM) theory. Compared with the experimental results obtained in our previous work, we suggest that the rearrangement of the further solvation shell could be important for the relaxation dynamics of the inhomogeneous spectral band width observed by means of transient hole-burning and time-resolved fluorescence spectroscopy.

I-S Developing Theories of Liquids and Liquid Mixtures

In the past few years, we have been concentrating our effort on building theories for chemical processes in solution. Our main concern in such study was to develop new theories which can describe “solvation” or “solvent effect” on chemical processes of interest by means of the statistical mechanics of liquids. A key to such development is the “RISM theory,” and many intriguing chemistry as well as physics have been investigated in our group using the theory at least in qualitative level. On the hand, we are also experiencing serious break down of the theory sometime as we try to explore new problems such as the gas-liquid phase transition, protein solution, and liquid-liquid mixtures.

In what follows, we describe our challenges to explore new problems related to liquids and liquid mixtures. The challenge inevitably includes methodological development in the statistical mechanics of liquids.

I-S-1 Integral Equations for Molecular Fluids Based on Interaction Site Model: Density-Functional Formulation

SUMI, Tomonari; IMAI, Takashi; HIRATA, Fumio

[*J. Chem. Phys.* **115**, 6653 (2001)]

An integral equation for rigid-body molecules with respect to site-density distribution function under arbitrary external fields is derived by density-functional theory. Using a grand canonical partition function of molecular systems, we extend original Percus’ idea to molecular fluids. The extended Percus’ idea provides a relation between site-site pair distribution function and site-density distribution function under an external field composed of the site-site interaction potentials of a molecule fixed at the origin. The site-density integral equation combined with the extended Percus' relation to molecular fluids gives a closure relation of reference interaction site model (RISM) equation. The site-site pair distribution functions of homonuclear diatomic Lennard-Jones fluids obtained by the integral equation agree well with those of Monte Carlo simulation.

I-S-2 A Replica Reference Interaction Site Model Theory for a Polar Molecular Liquid Sorbed in a Disordered Microporous Material with Polar Chemical Groups

KOVALENKO, Andriy; HIRATA, Fumio

[*J. Chem. Phys.* **115**, 8620 (2001)]

We develop a replica generalization of the reference interaction site model (replica RISM) integral equation theory to describe the structure and thermodynamics of quenched-annealed systems comprising polar molecular species. It provides a successful approach to realistic models of molecular liquids, and properly allows for the effect of a quenched disordered matrix on the sorbed liquid. The description can be extended to an electrolyte solution in a disordered material containing charged chemical functionalities that determine its adsorption character. The replica RISM equations are complemented with the HNC closure and its partial linearization (PLHNC), adequate to ionic and polar molecular liquids. In these approximations, the excess chemical potentials are derived in a closed analytical form. We extend the description to a quenched-annealed system with soft-core interaction potentials between all species, in which the liquid and matrix equilibrium distributions are characterized in general by two different temperatures. The replica RISM/PLHNC-HNC theory is applied to water sorbed in a quenched disordered microporous network of atoms associated into interconnected branched chains, with activating polar groups grafted to matrix chains. The results are in qualitative agreement with experiment for water confined in disordered materials.

I-S-3 First-Principles Realization of a van der Waals-Maxwell Theory for Water

KOVALENKO, Andriy; HIRATA, Fumio

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

We generalize the van der Waals-Maxwell description of the fluid phase diagram to account for chemical specificities of polar molecular fluids, such as hydrogen bonding in water. The theory is based on the reference interaction site model (RISM) integral equation method in the partially linearized hypernetted chain (PLHNC) approximation. The predictions for the liquid-vapor coexistence of water are in qualitative agreement with molecular simulations. The theory can be extended to electrolyte as well as non-electrolyte solutions, and to ionic liquids.

I-S-4 Thermochemistry of Solvation: A Self-Consistent Three-Dimensional Reference Interaction Site Model Approach

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([1]Univ. Utah)

[*J. Chem. Phys.* **113**, 7458 (2000)]

We developed a self-consistent three-dimensional reference interaction site model integral equation theory with the molecular hypernetted chain closure (SC-3D-RISM/HNC) for studying thermochemistry of solvation of ionic solutes in a polar molecular solvent. It is free from the inconsistency in the positions of the ion-solvent site distribution peaks, peculiar to the conventional RISM/HNC approach and improves the predictions for the solvation thermodynamics. The SC-3D-RISM treatment can be readily generalized to the case of finite ionic concentrations, including the consistent dielectric corrections to provide a consistent description of the dielectric properties of ion-molecular solution. The proposed theory is tested for hydration of the Na^+ and Cl^- ions in ambient water at infinite dilution. An improved agreement of the ion hydration structure and thermodynamics with molecular simulation results is found as compared to the conventional RISM/HNC treatment.

I-T Charge-Transfer Excitations and Fluctuations in Quasi-One-Dimensional Organic Conductors

i) In quasi-one-dimensional segregated-stack organic charge-transfer complexes with a quarter-filled band, $(TMTTF)_2X$ and $(TMTSF)_2X$, variation of physical properties under physical or chemical pressure can be viewed as a dimensional crossover. We have already studied how the crossover of the normal-phase properties above the phase transition temperatures to three-dimensional ones is achieved by increasing intermolecular overlaps between the neighboring chains and/or reducing electron correlation. The umklapp process has been essential to the confinement of fermions and to the antiferromagnetic long-range order. However, it was difficult to treat excitation spectra by the previous analytic approaches. Now a numerical approach is employed to deal with the dimensional crossover experimentally observed in excitation spectra. ii) In quasi-one-dimensional mixed-stack organic charge-transfer complexes with a half-filled band, neutral-ionic phase transitions with decreasing temperature, with increasing pressure, or with irradiation of light have been extensively investigated. Recently, complexes with inter-columnar networks have been synthesized and examined. Among them, the (BEDO-TTF)(Cl_2TCNQ) complex shows an unusual phase transition accompanied with a sharp drop in the magnetic susceptibility. A completely new mechanism for the transition from the ionic to neutral phases is proposed and numerically investigated. Even in the conventional, quasi-one-dimensional complex, TTF-CA, time-resolved spectroscopic data just after the irradiation of light are accumulated during the photo-induced phase transition. We also study the dynamics of neutral and ionic domains in such a non-equilibrium condition.

I-T-1 Intra- and Inter-Chain Excitations near a Quantum Phase Transition in Quasi-One-Dimensional Conductors

YONEMITSU, Kenji

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

We study intra- and inter-chain excitation spectra near a quantum phase transition in a spinless fermion model on a two-leg ladder at half filling by the finite-temperature density-matrix renormalization-group method. Above a critical strength of intrachain nearest-neighbor repulsion, a gap appears, accompanied with a long-range order of density modulation in the checkerboard pattern at zero temperature. The intrachain excitation spectra do not change so much in the gapless phase below the critical strength, while the interchain excitation spectra are considerably altered by the intrachain repulsion even in the gapless phase. Relevance to the optical conductivity in quasi-one-dimensional electron systems is suggested.

I-T-2 Collective Excitations and Confinement in the Excitation Spectra of the Spinless-Fermion Model on a Ladder

YONEMITSU, Kenji

[*Phys. Rev. B* submitted]

Intra- and inter-chain, local charge-transfer excitation spectra and the single-particle density of states are calculated by the finite-temperature density-matrix renormalization-group method in the spinless-fermion model on a ladder with varying intra-chain nearest-neighbor repulsion and with small inter-chain transfer integral at and near half filling. Collective excitations govern the low-energy intra-chain spectra, while only individual local excitations are present in the inter-chain spectra. As a consequence, at half filling, the intra-chain repulsion affects the inter-chain spectra more sensitively than the intra-chain spectra. Meanwhile, the inter-chain transfer integral affects the intra-chain spectra more sensitively through modifying the density-density correlation strength. The difference between the intra- and inter-chain spectra in the insulating phase can be interpreted from the viewpoint of confinement. It is found that the doping dependence of the local charge-transfer excitation spectra is similar to the dependence on the inter-chain transfer integral. It is because the inter-chain motion of fermions is not band-like but incoherent. Similarities between these findings and the experimentally observed, optical conductivity spectra in the quasi-one-dimensional organic conductors, $(TMTSF)_2X$, are pointed out.

I-T-3 Quantum and Thermal Charge-Transfer Fluctuations for Neutral-Ionic Phase Transitions in the One-Dimensional Extended Hubbard Model with Alternating Potentials

YONEMITSU, Kenji

[*Phys. Rev. B* submitted]

Effects of quantum and thermal fluctuations on transitions between the ionic phase and the neutral phase are studied by applying the finite-temperature density-matrix renormalization-group method to the one-dimensional extended Hubbard model with alternating potentials at half filling. Charge-transfer fluctuations lower the energy of the neutral phase more than that of the ionic phase, which is in contrast to the spin fluctuations favoring the ionic phase. As a consequence, with increasing intermolecular overlap between the neighboring donor and acceptor sites, we expect a spin-fluctuation-induced transition from the neutral phase to the ionic phase, and a charge-transfer-fluctuation-induced transition from the ionic phase to the neutral phase, near the phase boundary. Relevance to a recently observed phase transition in a new class of mixed-stack charge-transfer complexes is discussed.

I-T-4 Photoexcitations and Domain-Wall Dynamics near Neutral-Ionic Transitions

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

Recently, time-resolved photoreflectance spectra of TTF-CA have been measured just after photoexcitations by several groups. They are useful for the understanding of dynamical processes in the photoinduced phase transition, *e.g.*, creation and propagation of domain walls between the neutral and ionic phases. Real-time dynamics of such domain walls is studied by numerically solving the time-dependent Schrödinger equation for a one-dimensional extended Peierls-Hubbard model within the unrestricted Hartree-Fock approximation. Since thermal lattice fluctuations would be regarded as random initial conditions for lattice displacements, we add static impurities to the chain as a first step. Domain walls are generated at these impurity sites by photoexcitations. It is found that motion of domain walls depend at the early stage on the strengths of impurities and the intensity of photoexcitations.

I-T-5 New Photoinduced Phenomenon in Polymers

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([1]Fudan Univ.; [2]Natl. Lab. Infrared Phys.; [3]Inst. Mater. Struct. Sci.)

[*Phys. Rev. A* in press]

Numerical simulation has shown that a polymeric molecule can possess a new photoinduced phenomenon, photoinduced polarization reversion, in which the electric dipole of the polymeric molecule is reversed by absorbing one photon. This paper provides an analytic theory by means of a response function to prove that a polymer with a bipolaron has a negative static polarizability and explains the physical origin of this new photoinduced phenomenon in detail. This paper also presents a dynamical calculation for the photoinduced polarization reversion, from which the relaxation time for the dipole reversion can be determined.

I-U Cooperation or Competition between Electron Correlation and Lattice Effects in One-Dimensional π-*d* Electron Systems

i) Quasi-one-dimensional π-*d* hybrid electron systems, $(DCNQI)_2M$, are known to show a metal-insulator transition originating from the collaboration of the Peierls (*i.e*., electron-lattice) and Mott (*i.e*., electron-electron) mechanisms, which is contrary to the MMX chains. Although stability of the insulator phase with lattice modulation of period three is known in a wide pressure range, *i.e*., in a wide range of the π-*d* level difference, its theoretical treatment was very difficult because of strong correlation and highly nonlinear lattice effects. Strong commensurability effects on the stability are investigated by extensive numerical calculations. Another phase found nearby is consistent with the tendency observed by recent experiments. ii) Various charge-ordered phases are found accompanied with different lattice modulation patterns in quasi-one-dimensional halogen-bridged binuclear metal complexes, which are often called MMX chains. The dependence of the charge ordering, the lattice distortion and the optical conductivity spectra on the ligand, the counter ion and the halogen ion has been explained by competition between electron-lattice and electron-electron interactions, that between site-diagonal and site-off-diagonal interactions, and that between short-range and long-range interactions.

I-U-1 Strong Commensurability Effect on Metal-Insulator Transition in $(DCNQI)_2Cu$

KUWABARA, Makoto[1]**; YONEMITSU, Kenji**
([1]Kobe Univ.)

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

$(DCNQI)_2Cu$ salts, which are one-dimensional π-*d* electron systems, show unique physical properties associated with hybridization between π bands of DCNQI molecules and *d* orbitals of Cu. The metal-insulator transition is regarded as a cooperative phenomenon due to the Peierls instability in the 1/3-filled π band and the Mott instability in the *d* orbitals, 5/6 of which are occupied. We study stability of three-fold lattice distortion in the insulating state of $(DCNQI)_2Cu$ by exactly diagonalizing a two-band Peierls-Hubbard model on the 6×2 lattice. Self-doping is essentially important and caused by strong commensurability pinning, which is a consequence of moderate coupling of DCNQI π electrons with lattice and strong correlation of Cu *d* electrons.

I-U-2 Optical Excitations in XMMX Monomers and MMX Chains

KUWABARA, Makoto[1]**; YONEMITSU, Kenji**

([1]Kobe Univ.)

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

We study optical excitations in $K_4[Pt_2(pop)_4X_2]$ monomers (X = Cl, Br, I), using an extended Hubbard model. We show that long-range transfer integrals and long-range Coulomb interactions are substantially large to reproduce the experimental results. Due to the strong long-range Coulomb interactions, it is expected that the optical conductivity spectra of the MMX chains have two peaks in the charge polarization phase.

I-U-3 Ground State Phases and Optical Properties in Extended Peierls-Hubbard Models for Halogen-Bridged Binuclear Metal Complexes

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[*J. Mater. Chem.* **11**, 2163 (2001)]

Mechanisms of a variety of charge and lattice ordered phases observed in halogen-bridged binuclear metal complexes are theoretically studied by applying the exact diagonalization and strong-coupling expansion methods to one- and two-band extended Peierls-Hubbard models. In $R_4[Pt_2(pop)_4I]_nH_2O$ [R = Na, K, NH_4, $(CH_3(CH_2)_7)_2NH_2$, *etc.*, pop = $P_2O_5H_2^{2-}$] containing charged MMX chains, three electronic phases are suggested by experiments. We find that the variation of the electronic phases originates not only from competition between site-diagonal electron-lattice and electron-electron interactions but also from competition between short-range and long-range electron-electron interactions. On the other hand, in $Pt_2(RCS_2)_4I$ (R = CH_3, n-C_4H_9) containing neutral MMX chains, a site-off-diagonal electron-lattice interaction and the absence of counter ions are found to be crucial to produce the recently found, ordered phase. The optical conductivity spectra are also studied, which directly reflect the electronic phases. Their dependence on the electronic phase and on model parameters is clarified from the strong-coupling viewpoint.

I-V Charge Order, Lattice Distortion and Magnetism in Two-Dimensional Organic Conductors and Metal-Complexes

i) Quasi-two-dimensional metal complexes, $Et_nMe_{4-n}Z[Pd(dmit)_2]_2$, have strong dimerization and two bands consisting of the HOMO and the LUMO, which have different degrees of anisotropy. The cation controls the relative magnitudes of inter-molecular overlaps between neighboring dimers. They were known from our previous calculations to effectively control the degree of magnetic frustration and consequently whether the ground state is antiferromagnetic or paramagnetic. In the previous analysis, the interaction strengths had to be assumed. Now close comparisons between the experimental and theoretical optical conductivity spectra enable us to quantitatively estimate the magnitudes of different interaction strengths. ii) Among quasi-two-dimensional organic conductors, the θ-phase compounds are known to show metal-insulator transitions accompanied with charge ordering. Although long-range Coulomb repulsion is generally believed to be essential to the paramagnetic charge-ordered phase, the optical conductivity spectra do not show an excitonic band expected from our previous calculations. Then additional interaction terms might be important for the charge-ordering transitions. In fact, $(BEDT\text{-}TTF)_2RbZn(SCN)_4$ that has a lattice-distorted ground state has a rather high transition temperature. Both numerical and analytic calculations indeed suggest that weak electron-lattice coupling plays an important role.

I-V-1 Optical Conductivity for Possible Ground States of Dimerized Two-Band $Pd(dmit)_2$ Salts

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

We have studied the optical conductivity for possible ground states of $Pd(dmit)_2$ salts, by exactly diagonalizing a two-band Hubbard model for a dimer. The one-dimer model is useful to reproduce the overall structure of the optical spectra, since the intra-dimer transfer integrals, Ah and Al, are an order of magnitude larger than the inter-dimer transfer integrals. Our results reproduce dominant peaks of the optical spectra measured by Tajima *et al.* and confirm their argument from the strong-coupling viewpoint. The peak position and the intensity are generally affected by electron-electron interactions. The interaction strengths are estimated and used in the estimation of effective exchange interaction strengths between dimers. The cation dependence of the magnetic properties is reconsidered.

I-V-2 Charge Ordering Patterns and Their Excitation Spectra in Two-Dimensional Charge-Transfer Compounds

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

Charge ordering (CO) states are found in the insulating phase of θ-$(BEDT\text{-}TTF)_2MM'(SCN)_4$ (M =

Rb, Cs, M’ = Zn, Co) by various experimental studies. In the CO states, the charge density is disproportionate and the spin degrees of freedom survive. We calculated the optical conductivity spectra of some CO states in the quarter-filled extended Hubbard model by use of the random phase approximation (RPA) on the basis of the Hartree-Fock (HF) states. If the intersite interactions are essential, an excitonic effect should be significant to affect the peak positions and the spectral shape. Such excitonic effect is included in the RPA. We chose the values of intersite interaction strengths as to reproduce the experimentally observed degree of charge transfer about 0.4 in the HF calculation for each CO pattern. The conclusion from the RPA calculation is consistent with the Tajima *et al.*’s result as regards the number of peaks depending on the CO patterns. The RPA calculation shows a strongly excitonic character in the spectral shapes. However, the experimental data have no excitonic peak but rather broad bands probably ascribed to the inter-band transitions. This fact indicates that the above nearest-neighbor interaction strengths are too strong to explain the spectral shapes. To resolve this contradiction, not only the intersite interactions but also other interactions, *e.g.*, electron-lattice interactions, would be needed.

I-V-3 Paramagnetic Charge-Ordered States by Cooperation of Coulomb Repulsion with Electron-Lattice Coupling

MORI, Michiyasu[1]; YONEMITSU, Kenji
([1]Tohoku Univ.)

Charge ordering is clearly seen below around 190 K in the slowly cooled θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$ sample, where the crystal structure slightly changes at the transition temperature. If the same sample is rapidly cooled, the charge ordering becomes obscure from the room temperature down to about 20 K. It had been theoretically suggested that the charge ordering originates from the intersite repulsion in this quarter-filled system. Then, we previously calculated the optical conductivity spectra in the random phase approximation and showed that an excitonic effect should be significant if the intersite interaction is really essential. However, the experimental data show no excitonic peak but rather broad bands, which indicate that the intersite interaction is insufficient for the charge ordering. An additional interaction would resolve the contradiction by cooperatively stabilizing the charge ordering. We exactly diagonalize the Hamiltonian with an electron-lattice interaction suggested by X-ray diffraction experiments and compare the results with the second-order perturbation theory from the strong-coupling limit. Weak electron-lattice coupling indeed enhances the effect of long-range Coulomb repulsion on the charge ordering, but keeps the paramagnetism.

I-W Vortices in the Mixed State of High-Temperature Cuprate Superconductors

To elucidate anomalous metallic properties around the high-temperature superconductivity in copper oxides has been one of the major challenges in condensed matter physics. The key issue is competing low-energy instabilities near the superconducting ground state, including antiferromagnetic, stripe, or flux instabilities. Theoretical controversy between the spin-liquid and the Fermi-liquid approaches to the issue is far from resolution. Among the spin-liquid approach, the SU(2) gauge theory recently attracts attention because the flux state predicted by it may be related with another theory or with some numerical calculations. A criterion of whether such approach is valid or not is given by whether its consequence can be experimentally detected or not. Now, atomic resolution scanning tunneling microscope (STM) techniques are well developed. Here, we propose a promising STM experiment to detect signature of the flux state around the superconducting vortex and discuss consequences of the hidden SU(2) gauge structure in underdoped cuprates.

I-W-1 Signature of the Staggered Flux State around a Superconducting Vortex in Underdoped Cuprates

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[*Phys. Rev. Lett.* **86**, 5365 (2001)]

Based on the SU(2) lattice gauge field formulation of the *t-J* model, we discuss possible signature of the unit cell doubling associated with the staggered flux (SF) state in the lightly doped spin liquid. Although the SF state appears only dynamically in a uniform *d*-wave superconducting state, a topological defect [SU(2) vortex] freezes the SF state inside the vortex core. Consequently, the unit cell doubling shows up in the hopping (χ_{ij}) and pairing (Δ_{ij}) order parameters of physical electrons. We find that whereas the center in the vortex core is a SF state, as one moves away from the core center, a correlated staggered modulation of χ_{ij} and Δ_{ij} becomes predominant. We predict that over the region outside the core and inside the internal gauge field penetration depth around a vortex center, the local density-of-states exhibits staggered peak-dip structure inside the V-shaped profile when measured on the bonds. The staggered peak-dip structure has its direct origin in the unit cell doubling associated with the SF core and the robust topological texture, which has little to do with the symmetry of the *d*-wave order parameter. Therefore the structure may survive the tunneling matrix element effects and easily be detected by STM experiment.