RESEARCH ACTIVITIES I
Department of Theoretical Studies

I-A Theoretical Study and Design of New Bonding, Structures, and Reactions

It is an important subject to develop molecules with novel bonding and structures. Thus, new bonds containing heavier atoms are investigated, which are the focus of interest as new building block for molecular design. In addition, cage-like molecules and clusters are investigated to characterize guest-host interactions, which serve as molecular containers and recognition. Efficient computational methods are also investigated to perform calculations of large molecular systems.

I-A-1 Theoretical Investigation of Triple Bonding between Transition Metal and Main Group Elements in (η^5-C_5H_5)$(CO)_2$M≡ER (M = Cr, Mo, W; E = Si, Ge, Sn, Pb; R = Terphenyl Groups)

TAKAGI, Nozomi; YAMAZAKI, Kentaro[1]; NAGASE, Shigeru
([1]Univ. Tokyo)

[*Bull. Korean Chem. Soc. (a special issue)* **24**, 832–836 (2003)]

To extend the knowledge of triple bonding between group 6 transition metal and heavier group 14 elements, the structural and bonding aspects of (η^5-C_5H_5)$(CO)_2$-M≡ER (M = Cr, Mo, W; E = Si, Ge, Sn, Pb) are investigated by hybrid density functional calculations at the B3PW91 level. Substituent effects are also investigated with R = H, Me, SiH_3, Ph, C_6H_3-2,6-Ph_2, C_6H_3-2,6-(C_6H_2-2,4,6-Me_3)$_2$, and C_6H_3-2,6-(C_6H_2-2,4,6-*i*Pr_3)$_2$.

I-A-2 Synthesis and Characterization of Cyclic Silicon Compounds of Fullerenes

WAKAHARA, Takatsugu[1]; KAKO, Masahiro[2]; MAEDA, Yutaka[3]; AKASAKA, Takeshi[1]; KOBAYASHI, Kaoru; NAGASE, Shigeru
([1]Univ. Tsukuba; [2]Univ. Electron-Communication; [3]Tokyo Gakugei Univ.)

[*Curr. Org. Chem.* **7**, 927–943 (2003)]

Organosilicon compounds are among the most important inter-element compounds, as exemplified by disilanes and polysilanes. Since the availability of C_{60} in preparatively useful quantities, the chemical functionalization has attracted considerable interest, which leads to new cyclic silicon compounds. It is experimentally and theoretically investigated how silylenes, which are derived from a variety of disilanes under thermal and photochemical conditions, react with fullerenes and endohedral metallofullerenes. Mono-, bis-, and even multi-silylation of fullerenes lead to a new class of silicon compounds that are useful in material applications.

I-A-3 Calculation of Packing Structure of Methanol Solid using Ab Initio Latice Energy at the MP2 Level

NAGAYOSHI, Kanade[1]; KITAURA, Kazuo[2]; KOSEKI, Shiro[3]; RE, Suyong; KOBAYASHI, Kaoru; CHOE, Yoong-Kee; NAGASE, Shigeru
([1]IMS and Osaka Prefecture Univ.; [2]AIST; [3]Osaka Prefecture Univ.)

[*Chem. Phys. Lett.* **369**, 597–604 (2003)]

An ab initio MO based lattice energy minimization method is applied to the calculation of packing structures of methanol crystal, α- and β-phases. The second order Møller-Plesset perturbation theory (MP2) is employed to calculate lattice energies. The lattice parameters optimized at the MP2/6-31G++G(*d*,*p*) level for α- and β-phases are in good and moderate agreement with the experimental values, respectively. The average relative errors of calculated cell lengths are 0.9 and 6.2% for α- and β-phases, respectively.

I-A-4 Computational Procedure of Lattice Energy using the Ab Initio MO Method

NAGAYOSHI, Kanade[1]; IKEDA, Tohru[2]; KITAURA, Kazuo[3]; NAGASE, Shigeru
([1]IMS and Osaka Prefecture Univ.; [2]Osaka Prefecture Univ.; [3]AIST)

[*J. Theor. Comput. Chem.* **2**, 233–244 (2003)]

Recently, we have proposed a computational procedure for calculations of lattice energies of molecular crystals using the *ab initio* MO method. This procedure does not use potential functions and is applicable to a variety of molecular crystals. The procedure has been successfully applied to calculation of packing structure of electron donor-acceptor complex, H_3N-BF_3, and hydrogen bonding crystal, CH_3OH. In this work, we present a full account of the computational procedure. This method is applied to the packing structure calculations of hydrocarbon crystals, C_2H_2, C_2H_4 and C_6H_6. The lattice parameters optimized at the MP2/6-311++G** level are in good agreement with the experimental values. The basis set dependence of the lattice constants is also discussed for several crystals.

I-A-5 $La_2@C_{80}$: Is the Circular Motion of Two La Atoms Controllable by Exohedral Addition?

KOBAYASHI, Kaoru; NAGASE, Shigeru; MAEDA, Yutaka[1]; WAKAHARA, Takatsugu[2]; AKASAKA, Takeshi[2]
([1]Tokyo Gakugei Univ.; [2]Univ. Tsukuba)

[*Chem. Phys. Lett.* **374**, 562–566 (2003)]

Density functional calculations are carried out for the $La_2@C_{80}$ derivatives to investigate whether the motion of metals encapsulated inside fullerenes is controlled by exohedral addition. It is shown that the three-dimensional random motion of two La atoms in $La_2@C_{80}$ can be restricted to the circular motion in a plane by attaching electron-donating molecules on the outer surface of the C_{80} cage. It is expected that the two-dimensional circular motion will help to induce a unique electronic or magnetic field.

I-A-6 A Theoretical Study of Spin Density Distributions and Isotropic Hyperfine Couplings of N and P atoms in $N@C_{60}$, $P@C_{60}$, $N@C_{70}$, $N@C_{60}(CH_2)_6$, and $N@C_{60}(SiH_2)_6$

KOBAYASHI, Kaoru; NAGASE, Shigeru; DINSE, Klaus-Peter[1]
([1]IMS and TU-Darmstadt)

[*Chem. Phys. Lett.* **377**, 93–98 (2003)]

Spin density distributions and isotropic hyperfine coupling constants of $N@C_{60}$, $P@C_{60}$, $N@C_{70}$, $N@C_{60}(CH_2)_6$, and $N@C_{60}(SiH_2)_6$ are theoretically investigated by testing B3LYP and MP2 methods for the free N and P atoms. When N is encapsulated inside C_{60}, the calculated spin density at nucleus N increases. In $P@C_{60}$, the corresponding increase is much larger. $N@C_{60}$ has a slightly larger spin density at N than $N@C_{70}$. These agree well with the observed isotropic hyperfine coupling constants. Upon addition of CH_2 groups on the $N@C_{60}$ cage, the spin density at N is slightly decreased. However, addition of SiH_2 groups increases significantly the spin density at the nitrogen nucleus.

I-A-7 Theoretical Identification of C_{20} Carbon Clusters

LU, Jing[1]; RE, Suyong; CHOE, Yoong-Kee; NAGASE, Shigeru; ZHOU, Yunsong[2]; HAN, Rushan[2]; PENG, Lianmao[2]; ZHANG, Xinwei[2]; ZHAO, Xiangeng[2]
([1]IMS and Peking Univ.; [2]Peking Univ.)

[*Phys. Rev. B* **67**, 125415 (7 pages) (2003)]

Free energies, electron affinities and vibrational modes are theoretically investigated for several C_{20} isomers. The dominant C_{20} species generated by vaporizing graphite is first clarified. It turns out to be the monocyclic ring, followed by a tadpole (a short chain attached to a monocyclic ring), linear chain, and a bicyclic ring. On this basis, the two recently synthesized C_{20} isomers [*Nature* **407**, 60 (2000)] may be exclusively attributed to fullerene and bowl structures. Therefore, the existence of the smallest fullerene and C_{20} bowl isomer appear to be fully confirmed.

I-A-8 Structural and Electronic Properties of Metal-Encapsulated Silicon Clusters in a Large Size Range

LU, Jing[1]; NAGASE, Shigeru
([1]IMS and Peking Univ.)

[*Phys. Rev. Lett.* **90**, 115506 (4 pages) (2003)]

Structural and electronic properties of metal-doped silicon clusters MSi_n (M = W, Zr, Os, Pt, *etc.*) in a large size range $8 \leq n \leq 20$ are theoretically investigated. In contrast to a recent experiment suggesting that a metal atom is encapsulated inside the Si_n cluster, we reveal that the formation of endohedral structures depends strongly on the size of silicon clusters. Two novel structures of chemically stable endohedral species are manifested. The suitable $M@Si_n$ building blocks of self-assembly materials vary in the range $10 \leq n \leq 16$. The thermodynamical magic numbers are found to coincide with the chemical magic numbers for five clusters.

I-A-9 Metal-Doped Germanium Clusters MGe_n at the Sizes of $n = 12$ and 10: Divergence of Growth Patterns from the MSi_n Clusters

LU, Jing[1]; NAGASE, Shigeru
([1]IMS and Peking Univ.)

[*Chem. Phys. Lett.* **372**, 394–398 (2003)]

Structural and electronic properties of metal-doped germanium clusters MGe_n (M = Hf, W, Os, Ni, and Zn) in the sizes of $n = 12$ and 10 are investigated using hybrid density functional theory calculations. It is found that the growth patters are different from those of $M@Si_n$ clusters, though the pure Ge_n and Si_n clusters have identical geometries in the two sizes. The MGe_{12} (M = W and Os) and $ZnGe_{12}$ clusters have endohedral distorted hexagonal prismatic and endohedral perfect icosahedral structures, respectively, and show higher chemical stability among these checked MGe_n clusters. This makes them attractive for cluster-assembled materials.

I-A-10 $Ca@C_{72}$ IPR and Non-IPR Structures; Computed Temperature Development of their Relative Concentrations

SLANINA, Zdenek[1]; KOBAYASHI, Kaoru; NAGASE, Shigeru
([1]IMS and Academia Sinica)

[*Chem. Phys. Lett.* **372**, 810–814 (2003)]

Relative concentrations of four isomers of $Ca@C_{72}$

(one species with isolated pentagons, two isomers with a pentagon-pentagon junction, one structure with a heptagon) are computed using the Gibbs energy in a broad temperature interval. It is shown that both isomers with pentagon-pentagon junction are relatively close in concentrations at higher temperatures while the structure with isolated pentagons comes as a minor isomer (though it is the highest in potential energy) and the structure with heptagon is always negligible.

I-A-11 Photochemical Bissilylation of C_{70} with Disilane

RAHMAN, G. M. Aminur[1]; MAEDA, Yutaka[2]; WAKAHARA, Takatsugu[2]; KAKO, Masahiro[3]; SATO, Soichi[2]; OKAMURA, Mutsuo[1]; AKASAKA, Takeshi[2]; KOBAYASHI, Kaoru; NAGASE, Shigeru
([1]Niigata Univ; [2]Univ. Tsukuba; [3]Univ. Electro-Communications)

[*ITE Lett. Batt. New Tech. Med.* **4**, 60–66 (2003)]

The photochemical reaction of C_{70} with disilane affords bisadducts and monoadducts as major and minor products, respectively, which are successfully isolated. Theoretical calculations are carried out to disclose the structural features. The reaction patterns are characterized by calculating spin density distributions. It is expected that the silicon derivatives will play an important role in material and catalytic applications.

I-A-12 Redox Properties of Carbosilylated and Hydrosilylated Fullerene Derivatives

WAKAHARA, Takatsugu[1]; RAHMAN, G. M. Aminur[2]; MAEDA, Yutaka[1]; KAKO, Masahiro[3]; SATO, Soichi[2]; OKAMURA, Mutsuo[2]; AKASAKA, Takeshi[1]; KOBAYASHI, Kaoru; NAGASE, Shigeru
([1]Univ. Tsukuba; [2]Niigata Univ; [3]Univ. Electro-Communications)

[*ITE Lett. Batt. New Tech. Med.* **4**, 67–73 (2003)]

Experimental results and theoretical calculations suggest that the electrochemical properties of fullerenes, such as reduction and oxidation potentials, are significantly modified by attaching exohedrally silicon atoms on carbon cages. Among these, hydrosilylation and carbosilylation of C_{60} are useful to produce electronegative fullerene derivatives. It is expected that the derivatives with highly low oxidation potentials will open up a new application of C_{60} as a unique electron-donor.

I-A-13 B3LYP/6-31G* Computations of $C_{60}F_{36}$ (*g*) Isomers

SLANINA, Zdenek[1]; BOLTALINA, Olga V.[2]; KOBAYASHI, Kaoru; NAGASE, Shigeru
([1]IMS and Academia Sinica; [2]Moscow State Univ.)

Three isomers of $C_{60}F_{36}$ have been known from experiment. Previous computations however suggested five low-energy isomers though different methods do not always agree on the separation energetics. The present B3LYP/6-31G* computations support the observation of just three species. However, the computed energetics must still be adjusted in order to reproduce the observed concentration ratios.

I-B Prediction of Protein Tertiary Structures and Protein Folding Problem

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 a 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 and to study the protein folding mechanism by directly folding proteins.

I-B-1 Molecular Dynamics of C-Peptide of Ribonuclease A Studied by Replica-Exchange Monte Carlo Method and Diffusion Theory

LA PENNA, Giovanni[1]; MITSUTAKE, Ayori[2]; MASUYA, Masato[3]; OKAMOTO, Yuko
([1]Natl. Res. Council, Inst. Macromol. Studies, Italy; [2]Keio Univ.; [3]Kagoshima Univ.)

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

Generalized-ensemble algorithm and diffusion theory have been combined in order to compute the dynamical properties monitored by nuclear magnetic resonance experiments from efficient and reliable evaluation of statistical averages. Replica-exchange Monte Carlo simulations have been performed with a C-peptide analogue of ribonuclease A, and Smoluchowski diffusion equations have been applied. A fairly good agreement between the calculated and measured ^{1}H-NOESY NMR cross peaks has been obtained. The combination of these advanced and continuously improving statistical tools allows the calculation of a wide variety of dynamical properties routinely obtained by experiments.

I-B-2 Multi-Overlap Simulations for Transitions between Reference Configurations

BERG, Bernd A.[1]; NOGUCHI, Hiroshi; OKAMOTO, Yuko
([1]Florida State Univ.)

[*Phys. Rev. E* in press]

We introduce a new procedure to construct weight factors, which flatten the probability density of the overlap with respect to some pre-defined reference configuration. This allows one to overcome free energy barriers in the overlap variable. Subsequently, we generalize the approach to deal with the overlaps with respect to two reference configurations so that transitions between them are induced. We illustrate our approach by simulations of the brainpeptide Met-enkephalin with the ECEPP/2 energy function using the global-energy-minimum and the second lowest-energy states as reference configurations. The free energy is obtained as functions of the dihedral and the root-mean-square distances from these two configurations. The latter allows one to identify the transition state and to estimate its associated free energy barrier.

I-C 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-C-1 Monte Carlo Simulations in Multibaric-Multithermal Ensemble

OKUMURA, Hisashi; OKAMOTO, Yuko

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

We propose a new generalized-ensemble algorithm, which we refer to as the multibaric-multithermal Monte Carlo method. The multibaric-multithermal Monte Carlo simulations perform random walks widely both in volume space and in potential energy space. From only one simulation run, one can calculate isobaric-isothermal-ensemble averages at any pressure and any temperature. We test the effectiveness of this algorithm by applying it to the Lennard-Jones 12-6 potential system with 500 particles. It is found that a single simulation of the new method indeed gives accurate average quantities in isobaric-isothermal ensemble for a wide range of pressure and temperature.

I-D Applications of the Zhu-Nakamura Theory to Electronically Nonadiabatic Chemical Dynamics

I-D-1 Trajectory Surface Hopping Approach to Conical Intersection System

MIL'NIKOV, Gennady V.; OLOYEDE, Ponmile[1]; NAKAMURA, Hiroki
([1]GUAS)

The Zhu-Nakamura theory was proved to work well within the TSH (trajectory surface hopping) scheme in the case of DH_2^+ which presents a typical example of crossing seam type chemical reactions. It was found that the classically forbidden nonadiabatic transitions which cannot be treated by the Landau-Zener theory play important roles. In the present work the similar kind of analysis is carried out for a triatomic model reaction system of conical intersection. By doing this we would like to establish a general TSH method applicable to high dimensional systems.

I-D-2 Incorporation of the Zhu-Nakamura Theory into the Frozen Gaussian Propagation Method

KONDORSKIY, Alexey[1]; NAKAMURA, Hiroki
([1]IMS and Lebedev Physical Inst., Russia)

A new semiclassical theory is developed by combining the Herman-Kluk semicalassical theory for adiabatic propagation on single potential energy surface and the semiclassical Zhu-Nakamura theory for nonadiabatic transition. The formulation with use of natural mathematical principles leads to a quite simple expression for the propagator based on classical trajectories and simple formulas are derived for overall adiabatic and nonadiabatic processes. The theory is applied to electronically nonadiabatic photodissociation processes: one-dimensional problem of H_2^+ in a cw laser field and two-dimensional model problem of H_2O in a cw laser field. The theory is found to work well for the propagation duration of several molecular vibrational periods and wide wave packet energy range. Although the formulation is made for the case of laser induced nonadiabatic process, it is straghtforwardly applicable to ordinary electronically nonadiabatic chemical dynamics.

I-E Theory of Nonadiabatic Transitions

I-E-1 Semiclassical Theory of Nonadiabatic Transitions between Asymptotically Degenerate States

OSHEROV, Vladimir I.[1]; USHAKOV, Vladimir G.[1]; NAKAMURA, Hiroki
([1]Inst. Chemical Physics, Russia)

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

The semiclassical analysis is carried out for a two-state model potential system, in which two asymptotically degenerate Morse type 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. The result for non-crossing case provides the analytical expression of nonadiabatic transition matrix and can be used in a more general multichannel problem involving the present type of asymptotic transitions.

I-E-2 Analytical Treatment of S-P Type Collisional Resonant Excitation Transfer

OSHEROV, Vladimir I.[1]; USHAKOV, Vladimir G.[1]; NAKAMURA, Hiroki
([1]Inst. Chemical Physics, Russia)

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

The analytical solution developed in the previous paper is applied to the S-P type collisional resonant excitation transfer between atoms. The corresponding cross-sections are calculated in the high energy approximation. Good agreement is obtained with the results calculated previously by Watanabe with use of the fully numerical integration of the time-dependent coupled differential equations. This indicates usefulness of the present analytical theory developed in our previous papers.

I-E-3 Analytic Solution to Wave Packet Dynamics in a Laser Field: The Case of Linear Chirp

NAKAMURA, Hiroki

[*Chem. Phys.* in press]

An analytical expression for the nonadiabatic transition probability is derived for the case that two linear potentials in coordinate space are coupled by a linearly chirped time-dependent laser field. This constitutes a solution to the wave packet dynamics in the high energy approximation. Numerical calculations are carried out to demonstrate the applicability of the formula.

I-E-4 Nonadiabatic Transition—An Origin of Mutability of This World

NAKAMURA, Hiroki

(In “Nonadiabatic Transitions in Quantum Systems,” Russian Academic Publishing House, to be published)

A brief review of the Zhu-Nakamura theory and a brief explanation how to use the theory are presented together with some numerical applications. Recent theoretical developments on the other types of nonadiabatic transitions such as non-crossing case, exponential potential model and transitions among asymptotically degenerate states are also briefly described. Further discussions are made on laser control of molecular processes, intriguing phenomenon of complete reflection, and its applications such as molecular switching and bound states in the continuum.

I-E-5 Semiclassical Theory for Quantum Defect Function of Diatomic Molecules

SOLOVEV, Evgeni A.[1]; NAKAMURA, Hiroki
([1]IMS and Macedonian Acad. Sci. and Arts, Macedonia)

[*J. Phys. B* **36**, 3697 (2003)]

The simple analytical expression for the quantum defect function $\Delta_{lm}(R)$ of diatomic molecule is derived with use of the uniform semiclassical approach including the effects of hidden-crossing. $\Delta_{lm}(R)$ is a function of the internuclear distance R and the effective charge at each nucleus which is again a function of R. Thus, in the case of homonuclear molecule this expression gives universal dependence on R. The derived expression is applied to H_2 molecule. The quantum defects are found to be in good agreement with the *ab initio* numerical data by Wolniewicz and Dressler (*J.Chem.Phys.* **100**, 444).

I-E-6 Non-Linear Landau-Zener Model for Photoassociation of Cold Atoms

ISHKANYAN, Artur[1]; NAKAMURA, Hiroki
([1]IMS and Engineering Cent. Armenian Natl. Acad. Sci., Armenia)

A basic nonlinear model of the two state problem generic in classical and bosonic field theories with a cubic nonlinearity is considered taking the photoassociation of an atomic Bose-Einstein condensate as a specific example. For the class of models with constant external field amplitude a general strategy for attacking the problem is developed based on the reduction of the initial system of equations for the semi-classical atom-molecule amplitudes to a nonlinear Volterra integral equation for the molecular probability. The first approximation term of a uniformly convergent series solution to the Landau-Zener problem is derived and an asymptotic expression for the nonlinear transition probability to the molecular state is established for the weak interaction regime.

I-E-7 Nonadiabatic Transitions Induced by a Laser Field

OSHEROV, Vladimir I.[1]; USHAKOV, Vladimir G.[1]; NAKAMURA, Hiroki
([1]Inst. Chemical Physic, Russia)

The analytical study is carried out for a basic non-adiabatic atomic collision problem of two quantum states coupled by a laser field. The exact semiclassical solution has been found for the resonant type transitions and in the low frequency laser field limit. The high frequency field limit has also been considered in pseudoenergy ridge approach by a matching method.

I-F Quantum Dynamics of Chemical Reactions

I-F-1 Chemical Reactions in the O(^1D) + HCl System I. Ab Initio Global Potential Energy Surfaces for the 1^1A’, 2^1A’, and 1^1A’’ States

NANBU, Shinkoh; AOYAGI, Mutsumi; KAMISAKA, Hideyuki[1]; NAKAMURA, Hiroki; BIAN, Wensheng[2]; TANAKA, Kiyoshi[3]
([1]GUAS; [2]IMS and Shandong Univ., China; [3]Hokkaido Univ.)

[*J. Theor. Comput. Chem.* **1**, 263 (2002)]

New global *ab initio* potential energy surfaces (PES) are presented for the low-lying 1^1A’, 1^1A’’ and 2^1A’ electronic states which are correlated to O(^1D) + HCl. These potential energy surfaces are computed by using the multi-reference configuration interaction method with the Davidson correction (MRCI + Q). The reference functions are constructed by the complete active space self-consistent field (CASSCF) calculations using the quadruple zeta + polarization basis set augmented with diffuse functions. The computations are carried out at about 5000 molecular conformations on each three-dimensional potential energy surface. The high accuracy of the computations is confirmed by a comparison with the available most accurate data for the ground state 1^1A’; thus the present work is the first report of the accurate potential energy surfaces for the two excited states. Three low-lying transition states on the excited surfaces, two (TS2 and TS4) on 1^1A’’ and one (TS3) on 2^1A’, are found. Since TS2 and TS3 are as low as 0.07 eV and 0.28 eV, respectively, and correlate to the OH($^2\Pi$) + Cl(^2P) product, these excited surfaces are expected to play quite important roles in the reaction dynamics. Possible effects of nonadiabatic couplings among the three PESs are also briefly discussed, although the nonadiabatic couplings have not yet been estimated. The quantum reaction dynamics in these three PESs are discussed in the second accompanying paper, Paper II.

I-F-2 Chemical Reactions in the O(^1D) + HCl System II. Dynamics on the Ground 1^1A' State and Contributions of the Excited (1^1A'' and 2^1A') States

KAMISAKA, Hideyuki[1]; NAKAMURA, Hiroki; NANBU, Shinkoh; AOYAGI, Mutsumi; BIAN, Wensheng[2]; TANAKA, Kiyoshi[3]
([1]GUAS; [2]IMS and Shandong Univ., China; [3]Hokkaido Univ.)

[*J. Theor. Comput. Chem.* **1**, 275 (2002)]

Using the accurate global potential energy surfaces for the 1^1A', 1^1A'', and 2^1A' states reported in the previous sister Paper I, detailed quantum dynamics calculations are performed for these three adiabatic surfaces separately for $J = 0$ (J: total angular momentum quantum number). Overall reaction probabilities for O + HCl → OH + Cl and H + ClO, the branching ratio between the two reactions, effects of the initial rovibrational excitation, and product rovibrational distributions are evaluated in the total energy region $E_{\mathrm{tot}} \leq 0.9$ eV. Significant contributions to the overall reaction dynamics are found from the two excited 1^1A'' and 2^1A' potential energy surfaces, clearly indicating the insufficiency of the dynamics only on the ground 1^1A' surface. The detailed dynamics on the excited surfaces are reported in the third paper of this series.

I-F-3 Chemical Reactions in the O(^1D) + HCl System III. Quantum Dynamics on the Excited (1^1A'' and 2^1A') Potential Energy Surfaces

KAMISAKA, Hideyuki[1]; NAKAMURA, Hiroki; NANBU, Shinkoh; AOYAGI, Mutsumi; BIAN, Wensheng[2]; TANAKA, Kiyoshi[3]
([1]GUAS; [2]IMS and Shangdong Univ., China; [3]Hokkaido Univ.)

[*J. Theor. Comput. Chem.* **1**, 285 (2002)]

Using the accurate global potential energy surfaces for the 1^1A'' and 2^1A' states reported in the previous sister Paper I, detailed quantum dynamics calculations are performed for these adiabatic surfaces separately for $J = 0$ (J: total angular momentum quantum number). In addition to the significant overall contributions of these states to the title reactions reported in the second Paper II of this series, quantum dynamics on these excited potential energy surfaces (PES) are clarified in terms of the PES topographies, which are quite different from that of the ground PES. The reaction mechanisms are found to be strongly selective and nicely explained as vibrationally nonadiabatic transitions in the vicinity of potential ridge.

I-F-4 Quantum Reaction Dynamics of Triatomic Systems in the Hyperspherical Elliptic Coordinates

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

The Hamiltonian expression for the case of general nonzero total angular momentum J is derived in the hyperspherical *elliptic* coordinates which present a powerful tool for analyzing heavy-light-heavy reactions. Implementation of scattering calculations is also discussed. Numerical demonstrations are made by taking the Cl + HD reaction as an example.

I-G Theory of Multi-Dimensional Tunneling

I-G-1 Practical Implementation of the Instanton Theory. II. Decay of Metastable State Through Tunneling

MIL'NIKOV, Gennady V.; NAKAMURA, Hiroki

[*J. Chem. Phys.* **117**, 10081 (2002)]

A new instanton theory for decay rate problem at zero temperature is presented. The canonically invariant expression for the lifetime of metastable state is derived. The theory is fully implemented by an effective numerical recipe to find the instanton trajectory and is applicable to any high dimensional systems.

I-G-2 Tunneling Splitting in Polyatomic Molecules: Application to Malonaldehyde

MIL'NIKOV, Gennady V.; YAGI, Kiyoshi[1]; TAKETSUGU, Tetsuya[2]; NAKAMURA, Hiroki; HIRAO, Kimihiko[1]
([1]Univ. Tokyo; [2]Ochanomizu Univ.)

[*J. Chem. Phys.* **119**, 10 (2003)]

We report an accurate and efficient full dimensional semiclassical *ab initio* method for calculation of energy level splitting due to tunneling in polyatomic system. The method is applied to 21-dimensional 9-atomic malonaldehyde molecule. The tunneling splittings obtained are $\Delta E(\mathrm{H}) = 21.2$ cm^{-1} for hydrogen atom transfer and $\Delta E(\mathrm{D}) = 3.0$ cm^{-1} for deuterium atom transfer, which are in excellent agreement with the experimental values of 21.6 cm^{-1} and, 2.9 cm^{-1} respectively. We believe that the present analysis gives the final solution to the longstanding problem.

I-G-3 Semiclassical Theory of Tunneling Splitting for Vibrationally Excited States

MIL'NIKOV, Gennady V.; NAKAMURA, Hiroki

The theory developed before for ground state tunneling splitting is extended to excited state. Both longitudinal and transverse excitation are considered and canonically in variant formulas of energy splitting are derived for the low-lying excited states. The multi-dimensional effect of oscillation of tunneling splitting against vibrational excitation can be nicely interpreted in terms of the local frequency.

I-G-4 A Novel Method to Determine Caustics on a Family of Classical Trajectories

OLOYEDE, Ponmile[1]; MIL'NIKOV, Gennady V.; NAKAMURA, Hiroki
([1]GUAS)

A new method to find caustics in multi-dimensional space is proposed. This is composed of the solution of the first order differential equations satisfied by $A_{ij} = \delta p_i/\delta q_j$ and the canonical transformation to avoid the divergence of this quantity. The repetitive use of this transformation enables us to detect closely-lying caustics. This method is useful in semiclassical treatment of chemical dynamics, since we can take into account the tunneling effects by restarting tunneling trajectories from caustics.

I-H Laser Control of Molecular Processes

I-H-1 Control of Molecular Processes by a Sequence of Linearly Chirped Pulses

NAGAYA, Kuninobu[1]; TERANISHI, Yoshiaki[2]; NAKAMURA, Hiroki
([1]GUAS; [2]Adv. Photon Res. Cent.)

[*J. Chem. Phys.* **117**, 9588 (2002)]

A new scheme of controlling molecular processes by a sequence of linearly chirped pulses is proposed and is applied to selective excitation of an energy level among closely lying ones and to complete electronic excitation of a diatomic molecule. The basic idea is quite different from the conventional ones utilizing chirped pulses in the sense that the present one does not rely on the idea of adiabatic rapid passage at all, but tries to control basic nonadiabatic transitions explicitly. Control of molecular processes can be achieved by controlling nonadiabatic transitions among Floquet (or dressed) states with use of the interference effects. The scheme can be formulated with use of the analytical theories of nonadiabatic transitions, and the proper control parameters can be estimated theoretically. Numerical demonstrations are provided to confirm the robustness of the method in comparison with the other conventional ones. Namely, the present scheme is shown to be stable against the variation of pulse area, complete and selective in population transfer, and fast to accomplish the transition. It is expected that the method can be applied to general multilevel systems and various types of wave packet dynamics. Its experimental realizability can also be expected, since linear chirping can now be relatively easily realized and manipulated.

I-H-2 Control of Photodissociation Branching Using the Complete Reflection Phenomenon: Application to HI Molecule

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([1]Adv. Photon Res. Cent.)

[*J. Theor. Comput. Chem.* **1**, 245 (2002)]

The laser control of photodissociation branching in a diatomic molecules is demonstrated to be effectively achieved with use of the complete reflection phenomenon. The phenomenon and the control condition can be nicely formulated by the semiclassical (Zhu-Nakamura) theory. The method is applied to the branching between $I(^2P_{3/2})(HI \rightarrow H + I)$ and $I^*(^2P_{1/2})$-$(HI \rightarrow H + I^*)$ formation, and nearly complete control is shown to be possible by appropriately choosing an initial vibrational state and laser frequency in spite of the fact that there are three electronically excited states involved. Numerical calculations of the corresponding wavepacket dynamics confirm the results.

I-H-3 Photodissociation of H_2^+ and HD^+ in an Intense Laser Field

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[*Phys. Rev. A* **66**, 05412 (2002)]

The photodissociation of H_2^+ and HD^+ by an intense laser pulse is investigated by solving the close-coupling equations without discretization. For the case of H_2^+ the photodissociation spectra are calculated under the condition mimicking the experimental one, and a fairly good agreement with the experiment is obtained. The uncertainty in the relative phases of initial states is found to lead to somewhat smoothing of the spectra, depending on the pulse length. It is also found that Raman-type transitions via intermediate dissociation continuum play an important role in determining the photodissociation spectra. This leads to a population increase of lower vibrational states and deforms the spectral profile. Dissociation from the lower vibrational states due to the bond softening is not strong enough. Photodissociation spectra and angular distribution are calculated also for HD^+ under the same conditions as in the H_2^+ case. The dipole transitions lead to additional structures in the energy spectra and angular distribution. There is a noticeable difference in the peak positions of dissociation spectrum for particles dissociated by the direct electronic-dipole transition and by the transitions via intermediate bound states. The photodissociation dynamics is further clarified by using the three-dimensional plots of the spectra as a function of the field intensity and frequency.

I-H-4 Control of Photodissociation by Using a Sequence of Chirped Pulses and Nonadiabatic Transitions

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Laser control of photodissociation is decomposed into two processes: (1) to shift an initial wave packet to an appropriate position on the ground potential curve, and (2) to let that packet transit to upper dissociative potential curve. The first step can be realized by using a sequence of chirped pulses and the second step is made possible by controlling the nonadiabatic transition between the dressed states.

I-I New Method of Scattering Calculation

I-I-1 Calculation of Resonances in a *dtμ* Molecule by the R-Matrix Method

MIL'NIKOV, Gennady V.; NAKAMURA, Hiroki

[*Phys. Rev. A* **67**, 034501 (2003)]

Using the spectral representation of Green's function, we calculate the density of states and extract parameters of resonances in the scattering system. The method is implemented for the resonances in the *dtμ* molecule below the *tμ* (n = 2) threshold.

I-J 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-J-1 Energy-Level Diagrams and Their Contribution to Two-Dimensional Spectroscopic Signal: Distinction between Relaxation Mechanisms by Two-Dimensional Spectroscopy

OKUMURA, Ko[1]; TANIMURA, Yoshitaka
([1]Ochanomizu Univ.)

[*J. Phys. Chem. B* (2003) in press]

We develop a Feynman rule for energy-level diagrams emphasizing their connections to the double-sided Feynman diagrams and physical processes in the Liouville space. Thereby, we completely identify such diagrams and processes contributing to the 2D response function in the Brownian oscillator model. We classify such diagrams or processes in quartets and numerically present signals separately from each quartet of diagrams or Liouville-space processes. We find that the signal from each quartet is distinctly different from the others; we can identify each peak in the frequency domain with a certain quartet. This provides the basis for analyzing and assigning actual 2D peaks and suggests the possibility of Liouville-space path-selective spectroscopy. As an application, we demonstrate an example in which two familiar homogeneous models of relaxation are distinguished by the existence or nonexistence of certain peaks on the 2D map; the appearance or disappearance of certain peaks is sensitive to the choice of coupling models. We also point out some confusion in the literature with regard to the inclusion of relaxation effects.

I-J-2 Two-Dimensional Spectroscopy for a Two-Dimensional Rotator Coupled to a Gaussian-Markoffian Noise Bath

SUZUKI, Yoko; TANIMURA, Yoshitaka

[*J. Chem. Phys.* **119**, 1650–1660 (2003)]

The dynamics of a system in the condensed phase are more clearly characterized by the multi-time correlation functions of physical observables than two-time ones. We investigate a two-dimensional motion of a rigid rotator coupled to a Gaussian-Markovian harmonic oscillator bath. The analytical expression of a four-time correlation function of a dipole that is the observable of the two-dimensional microwave or infrared spectroscopy is obtained from a generating functional approach. 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. For the weakly damped case, the result predicts an echo-like signal that can be explained by the Liouville space path ways. The two-dimensional spectra are more sensitive to the noise effects than the one-dimensional (linear-absorption) spectra, which mean two-time correlation functions of dipole. It is because the effects of the initial thermal distribution are cancelled through the higher-order optical transition process in the two-dimensional spectroscopy, while such thermal effects determine the profile of the line shape in the one-dimensional spectroscopy. The two-dimensional spectrum reveals three peaks corresponding to transition processes between the rotational energy levels even in the damped case, which cannot be observed in the one-dimensional spectroscopy. For the strongly damped case, the two-dimensional spectra reveal peaks that arise from the strongly damped motion and librational motion caused by the strong coupling between the system and the heat bath oscillators with narrow band spectral distribution. Whereas the effects of these motions are shown in the bimodal line of the one-dimensional spectroscopy, the profile of the two-dimensional spectrum clearly implies the origin of these two peaks.

I-J-3 Two-Dimensional Vibrational Spectroscopy of a Double Minimum System in a Dissipative Environment

KHÜN, Oliver; TANIMURA, Yoshitaka

[*J. Chem. Phys.* **119**, 2155–2164 (2003)]

A dissipative bistable system presents the simplest model to describe condensed phase reaction dynamics. Using a quantum master equation approach to calculate multitime dipole correlation functions we demonstrate how the dissipative dynamics can be characterized by time-resolved third-order infrared spectroscopy. Thereby we incorporate bilinear and linear–quadratic system–bath interaction into the Redfield relaxation tensor. Investigating equilibrium and nonequilibrium initial conditions for a symmetric system it is shown that bath-induced coherence transfer can have a dramatic influence on the two-dimensional signals. This occurs when the inverse of the ground state tunneling splitting is of the order of the coherence transfer time.

I-K Simulation and Dynamics of Real Molecular Systems

Accurate quantum computational chemistry has evolved dramatically. The size of molecular systems, which can be studied accurately using molecular theory is increasing very rapidly. Theoretical chemistry has opened up a world of new possibilities. It can treat real systems with predictable accuracy. Computational chemistry is becoming an integral part of chemistry research. Theory can now make very significant contribution to chemistry. The project focuses on the theoretical development in methodologies for the study of molecular electronic structures. We are aiming at developing accurate molecular theory on systems containing hundreds of atoms. We have continued our research in the following three directions: (i) development of new *ab initio* theory, particularly multireference based perturbation theory, (ii) development of exchange and correlation functionals in density functional theory, and (iii) development of molecular theory including relativistic effects.

I-K-1 UTChem—A Program for *Ab Initio* Quantum Chemistry

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[*Computational Science—ICCS 2003, Lecture Notes in Computer Science*, Springer, 84–95 (2003)]

Present molecular quantum theory is highly sophisticated, and has evolved dramatically. Software forms a basis for computational chemistry. However, it is not an easy task for an individual/group to develop a comprehensive new program package in *ab initio* quantum chemistry from scratch. Several years ago, we decided to accept this challenge. In view of the availability of such good programs as Gaussian, Gamess, Molcas, NWChem, *etc*., one may question the relevance of a new program package. We have three arguments for our project. (1) First, we believe that healthy competition is very important in science. (2) Second, we can have a good harvest by doing research using other programs, but it is an abortive flower. We could not make a true breakthrough if we were circumscribed by current software limitations. (3) Third, in spite of the excellent performance of other programs, there are important and powerful methods that others cannot yet handle. We have developed new methodologies in quantum chemistry, particularly the multireference-based perturbation theory for describing chemical reactions and excited states, relativistic molecular theory to treat heavy elements, parameter-free (less) exchange and correlation functionals in DFT, highly efficient algorithms for calculating molecular integrals over generally contracted Gaussians, *etc*. UTChem is a research product of our work to develop new and better theoretical methods in quantum chemistry. Most of the codes have been developed recently by Hirao's group at the University of Tokyo. The basic philosophy behind UTChem is to develop methods that allow an accurate and efficient computational chemistry of electronic structure problems for molecular systems in both the ground and excited states. UTChem also contains codes for well-developed methods such as MPn, CI, CC, *etc*., which are standard in most quantum chemistry programs. We are aiming ultimately at better performance than other programs. UTChem will soon be ready for distribution. Here you will be able to see the features of UTChem. UTChem contains a large number of improvements and some interesting new features, which others cannot match.

I-K-2 Douglas-Kroll Transformation to the Relativistic Many-Electron Hamiltonian

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[*J. Chem. Phys.* **119**, 4105–4111 (2003)]

A new generalized Douglas-Kroll (DK) approach has been proposed for the relativistic many-electron Hamiltonian including the electron-electron interaction. In order to consider the higher-order DK transformation to the two-electron interaction, the present approach adopts the effective one-electron potential in the Dirac-Hartree-Fock (DHF)/Dirac-Kohn-Sham (DKS) operator as an expansion parameter in the DK transformation. Its numerical performance is tested for the atomic Hg and molecular HAt and At_2 systems. The third-order DK transformation to both one-electron and two-electron Hamiltonians, which is the highest level of theory treated in this study, gives excellent agreement with the four-component relativistic approach. The first-order DK correction to the two-electron interaction is proved to be satisfactory for both atomic and molecular systems.

I-K-3 A Four-Index Transformation in Dirac's Four-Component Relativistic Theory

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[*J. Chem. Phys.* submitted]

A four-index transformation from atomic orbitals to molecular orbitals is an essential first step in any calculation that aims to account for correlation effects. An efficient integral transformation program based on the four-component spinors resulting from the Dirac-

Hartree-Fock method is implemented in our program package, *UTChem*. By adopting generally contracted spherical harmonic Gaussian-type spinors, the number of small-component basis functions is reduced to about one half compared with commonly used kinetically balanced basis sets. The decrease in basis functions permits an efficient integral transformation. The present integral transformation program is four to eight times faster than the pioneering programs of MOLFDIR and DIRAC. As illustrative examples, the singles and doubles coupled-cluster methods with and without perturbative triples [CCSD, CCSD(T)] are applied to the ground state of thallium hydride. The computed spectroscopic constants are in good agreement with experiment.

I-K-4 Recent Advances in Multireference-Based Perturbation Theory

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[*Bull. Korean Chem. Soc.* **24**, 812–816 (2003)]

Accurate *ab initio* computational chemistry has evolved dramatically. In particular, the development of multireference-based approaches has opened up a completely new area, and has had a profound impact on the potential of theoretical chemistry. Multireference-based perturbation theory (MRPT) is an extension of the closed-shell single reference Møller-Plesset method, and has been successfully applied to many chemical and spectroscopic problems. MRPT has established itself as an efficient technique for treating nondynamical and dynamical correlations. Usually, a complete active space self-consistent field (CASSCF) wave function is chosen as a reference function of MRPT. However, CASSCF often generates too many configurations, and the size of the active space can outgrow the capacity of the present technology. Many attempts have been proposed to reduce the dimension of CASSCF and to widen the range of applications of MRPT. This review focuses on our recent development in MRPT.

I-L Theoretical Studies of Quantum Effects in Chemical Reactions

Although the study of quantum mechanical effects in chemical reactions has its long standing history, quantitative understandings of the importance of quantum effects in reactions have not been achieved. We investigate quantum effects, tunneling, resonances, interference, and electronically nonadiabatic transitions, in simple reaction systems by means of various theoretical approaches, including quantum reactive scattering methods, semiclassical dynamical methods, and classical trajectory methods.

I-L-1 Ab Initio Calculations of Low-Lying Potential Energy Surfaces of the HHeF System

TAKAYANAGI, Toshiyuki
(IMS and JAERI)

[*Chem. Phys. Lett.* **371**, 675 (2003)]

The low-lying singlet potential energy surfaces for the HHeF system have been calculated using the ab initio electronic structure method at the multireference configuration interaction level of theory. It is found that the interaction of helium with HF($B^1\Sigma^+$) in the ion-pair electronically excited state is attractive in a wide rage of the orientation angle and that the helium atom strongly stabilize the ion-pair HHe^+F^- complex on the $3^1A'$ surface, which is asymptotically correlating to the HF($B^1\Sigma^+$) state. We also found that the electronically nonadiabatic coupling between the $1^1A'$ ground state and $3^1A'$ state plays an essential role in the topographical features of these two surfaces.

I-L-2 Photodissociation of Cl_2 in Helium Clusters: An Application of Hybrid Method of Quantum Wavepacket Dynamics and Path Integral Centroid Molecular Dynamics

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([1]IMS and JAERI; [2]JAERI)

[*Chem. Phys. Lett.* **372**, 90 (2003)]

The photodissociation dynamics of Cl_2 embedded in helium clusters is studied by numerical simulation with an emphasis on the effect of quantum character of helium motions. The simulation is based on the hybrid model in which Cl–Cl internuclear dynamics is treated in a wavepacket technique, while the helium motions are described by a path integral centroid molecular dynamics approach. It is found that the cage effect largely decreases when the helium motion is treated quantum mechanically. The mechanism is affected not only by the zero-point vibration in the helium solvation structure, but also by the quantum dynamics of helium.

I-L-3 Theoretical Simulations on Photoexcitation Dynamics of the Silver Atom Embedded in Helium Clusters

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([1]JAERI; [2]IMS and JAERI)

[*J. Chem. Phys.* **119**, 5478 (2003)]

Quantum molecular dynamics simulations have been performed to study the photoexcitation $Ag(5p^2P_J) \leftarrow Ag(5s^2S_{1/2})$ in size-selected helium clusters considering electronically nonadiabatic transitions. We employed the hybrid method in which the electronic degree of freedom of $Ag(^2P)$ was treated quantum mechanically while the motions of helium atoms were described by the semiclassical path integral centroid molecular dynamics method in order to take the quantum fluctuation effect into account. It has been found that the dynamics after photoexcitation is dominantly nonadiabatic in all cluster sizes studied, and that nonadiabatic transitions are enhanced by quantum fluctuation of helium motions. Most of the photoexcited AgHen clusters decompose into an isolated Ag atom and free helium atoms within several picoseconds. However, Ag^*He_n ($n = 1 \sim 5$) exciplex formation was also found to occur for all helium cluster sizes studied, although this process is found to be minor.

I-M Molecular Vibrations and Intermolecular Interactions in Condensed Phases

In this project, intermolecular interactions and their effects on molecular vibrations in condensed phases are analyzed theoretically to clarify the relation between the structures and dynamics of the systems and the frequency- and time-domain spectroscopic features. Specifically, (1) the resonant transfer of vibrational excitations, vibrational dephasing, and their competition in liquids and biomolecules and (2) the relation between electronic structural features of molecules and intermolecular interactions are analyzed with great emphasis.

I-M-1 The Role of Atomic Quadrupoles in Intermolecular Electrostatic Interactions of Polar and Nonpolar Molecules

TORII, Hajime
(IMS and Shizuoka Univ.)

[*J. Chem. Phys.* **119**, 2192–2198 (2003)]

For the purpose of getting insight into the reason for the anomalous vibrational frequency shifts observed in some usually used solvents for a mode that has a large dipole derivative, the role of atomic quadrupoles in intermolecular electrostatic interactions is studied for some halogen-containing molecules (CX_4, HX, and X_2 with X = F, Cl, and Br), CH_4, CO_2, and CS_2. From the fitting to the electrostatic potentials around the molecules, large atomic quadrupoles are obtained for the chlorine, bromine, and sulfur atoms, suggesting that the atomic quadrupolar effect is important for electrostatic interactions around covalently bonded atoms on the third and higher rows in the periodic table. Taking the case of the chlorine atoms as an example, the electron densities inside the atoms in CCl_4, HCl, and Cl_2 are examined. It is found that these electron densities are highly anisotropic. This anisotropy in electron densities is reasonably explained by the forms of the occupied molecular orbitals, and is considered to be the electronic structural origin of the large atomic quadrupoles.

I-M-2 Pressure Dependence of the Liquid Structure and the Raman Noncoincidence Effect of Liquid Methanol

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(IMS and Shizuoka Univ.)

[*Pure Appl. Chem.* in press]

Pressure dependence of the liquid structure and the Raman noncoincidence effect of liquid methanol is examined with the combination of molecular dynamics (MD) simulations and the intermolecular resonant vibrational interactions determined by the transition dipole coupling (TDC) mechanism (MD/TDC method). It is shown that the observed decrease of the Raman noncoincidence ν_{NCE} of the CO stretching band with increasing density reported in the literature is quantitatively reproduced by the present calculation. As the density increases, the hydrogen bonds get slightly shorter, but molecules belonging to different hydrogen-bond chains get closer to each other to a greater extent. This anisotropic change in the liquid structure is the reason for the behavior of ν_{NCE}. It is also shown that the concentration dependence of ν_{NCE} in the methanol/CCl_4 binary mixtures reported in a previous study and the pressure dependence of ν_{NCE} in methanol may be described in a consistent way as a function of the number density of methanol in the liquid systems.

I-M-3 Extent of Delocalization of Vibrational Modes in Liquids as a Result of Competition between Diagonal Disorder and Off-Diagonal Coupling

TORII, Hajime
(IMS and Shizuoka Univ.)

The changes in the extent of delocalization of vibrational modes in liquids arising from the competition between diagonal disorder and off-diagonal coupling in the vibrational exciton picture are examined theoretically. Calculations of vibrational modes and polarized Raman spectra are carried out on a model liquid system, in which spherical particles interact with each other by the Lennard-Jones and dipole-dipole interactions, and a one-dimensional oscillator (representing a vibrational degree of freedom) with a transition dipole and a Raman tensor is buried in each particle. The diagonal disorder is assumed to be in a Gaussian form, and the transition dipole coupling is introduced as the off-diagonal coupling in the vibrational Hamiltonian. The magnitude of the Raman noncoincidence effect (NCE), which is the phenomenon that the vibrational frequency positions of the isotropic and anisotropic components of a Raman band do not coincide and is often used as an experimental measure of the delocalization of vibrational modes, is calculated. In addition, two theoretical measures of the delocalization of vibrational modes are introduced, and their changes with the thermodynamic state of the liquid, the diagonal disorder, and the strength of the off-diagonal coupling are examined. It is shown that the extent of delocalization of vibrational modes is correlated with the “NCE detectability,” defined as the ratio of the magnitude of the NCE and the isotropic or anisotropic Raman band width. This result indicates that the extent of delocalization of vibrational modes in a vibrational band that shows the NCE may be estimated from the observed spectral profile of the band. The size of the space in which vibrational spectra can probe structural formation is also discussed.

I-N 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-N-1 Enthalpy and Entropy Decomposition of Free-Energy Changes for Side-Chain Conformations of Asparatic Acid and Asparagine in Acidic, Neutral, and Basic Aqueous Solutions

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[*J. Phys. Chem. B* **106**, 12336 (2002)]

Trans and gauche conformational equilibria in the side chains of aspartic acid (Asp) and asparagine (Asn) were investigated by measuring the vicinal spin-spin coupling constants of ^{1}H NMR in acidic, neutral, and basic aqueous solutions over a wide range of temperature (5–90 ˚C). The standard free-energy changes ΔG^0 were obtained for the trans to gauche conformational variations on the C_α–C_β bond with respect to the α-carboxyl group and the β-carboxyl group in Asp (β-amide in Asn) and were decomposed into enthalpic ΔH^0 and entropic-$T\Delta S^0$ components. The hydration of ionic and polar groups in Asp competes against the large intramolecular electrostatic repulsion energy and stabilizes the gauche more than the trans conformer in correspondence to a larger degree of separation of positive and negative partial charges. In the neutral solutions, where both the carboxyl groups are negatively ionized, the hydration part even overwhelms the intramolecular repulsion and leads to a negative ΔH^0. The fact that the hydration almost cancels the intramolecular electrostatic repulsion contradicts the widely accepted view that the trans preference in the conformational equilibrium is due to the intramolecular repulsion between α-CO_2- and β-CO_2- (or β-$CONH_2$).

I-N-2 Theoretical Study on Electronic and Solvent Reorganization Processes Associated with a Charging Process of Organic Compounds: I. Molecular and Atomic Level Description of Solvent Reorganization

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([1]Kyoto Univ.; [2]Tohoku Univ.)

[*J. Chem. Phys.* **119**, 2753 (2003)]

Electronic and solvation structures of *N*,*N*-dimethylaniline (DMA) in acetonitrile are examined by means of the ab initio reference interaction site model—self-consistent field (RISM-SCF) theory coupled with the method to evaluate nonequilibrium solvation free energy developed by Chong *et al*. [*J. Phys. Chem.* **99**, 10526 (1995)]. The key quantities characterizing the solvation process, free energy profile governing the solvent fluctuations and solvent reorganization, are evaluated from the first principle. A new scheme, which enables us to partition solvent reorganization into atomic contributions in the solute molecule, is proposed and used to analyze the process in atomic level. We found that the linear response approximation holds well and the overall observable, λs is not much affected by solute geometry, while the individual atomic contribution is significantly changed, especially, by the wagging motion of the amino group.

I-N-3 A Quantum Solute-Solvent Interaction Using Spectral Representation Technique Applied to the Electronic Structure Theory in Solution

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[*J. Chem. Phys.* **119**, 6663 (2003)]

In this paper, we present a new approach to treat the electronic structure of a molecule in solution. Unlike the hybrid-type method such as the reference interaction site model self-consistent-field(RISM-SCF) theory, the new approach describes not only the electronic structure of solute but also solute-solvent interactions in terms of the quantum chemistry based on the Hartree-Fock frozen density formulation. In the treatment, the quantum effect due to solvent, including exchange repulsion, is projected on to the solute Hamiltonian using the spectral representation method. The solvent distribution around the solute is handled by the integral equation theory of liquids. As illustrative applications of the approach, the electronic and solvation structure of noble atoms, neon and argon, in liquid neon are studied. We also investigate the electronic structure of an excess electron in liquid helium. The preliminary results demonstrate that the quantum mechanical effect on the electronic and solvation structure of the solute due to solvent molecules is successfully represented by the new method.

I-N-4 Interplay between the Repulsive and Attractive Interaction and the Spacial Dimensionality of an Excess Electron in a Simple Fluid

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[*J. Theor. Comput. Chem.* **2**, 129 (2003)]

The behavior of an excess electron in a one, two and three dimensional classical liquid has been studied with the aid of Chandler, Singh and Richardson (CSR) theory [*J. Chem. Phys.* **81**, 1975 (1984)]. The size or dispersion of the wavepacket associated with the solvated electron is very sensitive to the interaction between the electron and fluid atoms, and exhibits complicated behavior in its density dependence. The behavior is interpreted in terms of an interplay among four causes: the excluded volume effect due to solvent, the pair attractive interaction between the electron and a solvent atom, the thermal wavelength of the electron (λ_e), a balance of the attractive interactions from different solvent atoms and the range of repulsive interaction between electron and solvent atom. Electron self-trapping behavior in all the dimensions has been studied for the same solvent-solvent and electron-solvent interaction potential and the results are presented for the same parameter in every dimension to show the comparison between the various dimensions.

I-O 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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1-O-1 Partial Molar Volume and Compressibility of a Molecule with Internal Degrees of Freedom

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Statistical mechanical expressions for the partial molar volume (PMV) and the partial molar compressibility (PMC) of a solute molecule with internal degrees of freedom are derived. The equilibrium PMV is expressed simply by the conformational ensemble average of PMV. The equilibrium PMC consists of two terms: the conformational ensemble average of PMC and the mean square fluctuation of PMV along conformational axis. As an illustrative application of the theory, the equilibrium PMV and PMC of butane in aqueous solution are calculated from the relations, in which the thermodynamic quantities of each conformer appearing in the relations are obtained by the RISM theory. The conformational ensemble average of PMC is the predominant contribution to the equilibrium PMC in this particular example. Possibility of shedding light on the protein conformation in terms of PMV and PMC is discussed.

1-O-2 A Density-Functional Theory for Polymer Liquids Based on Interaction Site Model

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The density-functional theory (DFT) for molecular fluids [*J. Chem. Phys.* **115**, 6653 (2001)] is extended to the case of polymer liquids. A system consisting of the ideal chains is employed as a reference system for the DFT, where many-body effects are considered as an effective field that acts on each site of the ideal chains. We derived a relation between the site-site pair distribution functions and the site-density distribution functions under a mean field arising from a single polymer molecule. An integral equation for the site-site pair distribution functions is obtained by the DFT, where the external field is taken to be the mean field. We propose an approximate expression of the intramolecular correlation functions for isolated single-polymer chains to take account for the excluded volume effects inside a polymer chain. The intramolecular correlation function considering the excluded volume effects was in qualitative agreement with those obtained from a simulation for liquid consisting of freely jointed tangent-soft-core chains. The site-density integral equation under the mean field, using the intramolecular correlation function, reproduces the simulation results for site-site pair distribution functions of the system of freely jointed tangent-soft-core chains.

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

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

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

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I-P-1 Solute-Structure Dependence of Solvation Dynamics Studied by Reference Interaction-Site Model Theory

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A combination of the reference interaction-site model theory and site-site Smoluchowski-Vlasov equation is applied to estimate the dynamic response function of the average-energy relaxation of the solute-solvent system, $S_S(t)$. We calculate $S_S(t)$ for 13 model solutes with different structure, from a simple ion to an octopole, in a polar solvent. The partial charges of the ions and multipoles are changed to investigate nonlinear character of $S_S(t)$. The ‘‘nonlinear character’’ we study here corresponds to the response of the solvent fluctuation after the sudden change of the solute charge-distribution. Our present results reveal that $S_S(t)$ depends on the molecular structure and charge distribution of the solute. $S_S(t)$ is decomposed into two parts: one corresponding to the optical mode of solvent, the other to the acoustic mode. We show that for multipoles the optical mode is responsible for the fast part of $S_S(t)$, while the acoustic mode plays an important role in the slower dynamics. The dual nature of $S_S(t)$ is essential for the nonlinearity of solvation dynamics.

I-P-2 Dielectric Relaxation Spectrum of Water Studied by the Site-Site Generalized Langevin/Modified Mode-Coupling Theory

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The dielectric relaxation spectrum of water is calculated from the site-site generalized Langevin/modified mode-coupling theory. The main part of the relaxation follows the Debye-type function, and a small deviation from the Debye relaxation is found on the high-frequency side. This tendency is consistent with recent experiments, although the absolute relaxation time does not agree with the experimental value quantitatively. The time-development of the longitudinal polarization function resembles the dielectric part of the memory function, and we consider that this is because the dielectric friction dominates the collective reorientation of the dipole moment of water. We performed calculations with different dielectric constants using the reference interaction-site model integral equation, and found that the large gap between the time-scales of the dielectric relaxation and the longitudinal polarization relaxation causes the Debye-type dielectric relaxation when the dielectric friction is dominant in the friction on the collective reorientation of the dipole moment. Namely, the longitudinal polarization relaxation is fast enough to be considered as a white noise to the dielectric relaxation process, so that the relaxation becomes a Markov process. The large gap between the two relaxation times originates from a large local field correction due to the large dielectric constant of water. It is also suggested that the deviation from the Debye relaxation at the high-frequency side is the manifestation of the slow memory caused by the long-time part of the longitudinal polarization relaxation in the low-wavenumber region.

I-P-3 Theoretical Study on the Molecular Motion of Liquid Water under High Pressure

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[*J. Chem. Phys.* **119**, 1021 (2003)]

The pressure effects on the molecular dynamics of liquid water are investigated using the site-site generalized Langevin/modified mode-coupling theory. The calculations are performed for temperatures from 273 to 373 K and densities from 0.9 to 1.2 g/cm^3. The static structure factor required as input is obtained from the reference interaction-site model/hypernetted chain integral equation. The shear viscosity, the dielectric relaxation time, the translational diffusion coefficient, and the first-rank reorientational relaxation times are evaluated. All these quantities show unusual pressure dependence in the low-density, low-temperature region in that the molecular mobility is enhanced by applying the pressure. The magnitude of the enhancement is larger on the reorientational motions than on the translational ones. These tendencies are consistent with experimental observations, although the quantitative agreement is not so good. An analysis of the theory indicates that the decrease in the dielectric friction on the collective polarization at small wavenumbers upon increasing pressure is the principal reason for the pressure-induced enhancement of the dielectric relaxation, and the decrease in the dielectric relaxation time affects other motions. The decrease in the dielectric friction is caused by the decrease in the number-density fluctuation around the low-wavenumber edge of the first-peak of the structure factor by compression. The comparison between the results for water and acetonitrile extracts two characteristic features of water that are important for the anomalous pressure effect on its molecular motion. The first one is the small collisional friction on the reorientation due to the spherical repulsive core, and the second one is the strong short-range Coulombic interaction caused by the formation of the hydrogen-bonding. A theoretical calculation on a model diatomic liquid consisting of oxygen and hydrogen atoms proposes that the above two characteristic properties of water are sufficient for the emergence of the anomalous pressure dependence. This conclusion is also supported by the molecular dynamics simulation performed on the same model diatomic liquid.

I-Q 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-Q-1 Compressibility of Tert-Butyl Alcohol-Water Mixture: The RISM Theory

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[*J. Theor. Comput. Chem.* **2**, 193 (2003)]

The isothermal compressibility χ_T of binary mixtures of water and *tert*-butyl alcohol (TBA) is calculated using the reference interaction site model (RISM) integral equation theory. The calculations are performed over the whole concentration from $x = 0$ to 1 and a wide temperature from $T = 283$ to 313 K ranges employing an extended point charge model for water and optimized site-site potentials for TBA molecules. The results obtained are compared versus available experimental data. It is demonstrated that, despite an approximate character of the model potentials and closure relation applied, the theory is able to reproduce qualitatively all main features of the x- and T-dependencies of χ_T inherent in real experiment. Such features include the decrease of compressibility with increasing T in the low TBA concentration limit x to 0 (pure water), and the increase of χ_T with rising T in the opposite regime x to 1 (pure alcohol); the presence of a concentration region where the function $\chi_T(x,T)$ does not depend much on T; as well as the existence of a minimum in χ_T with respect to x at each given T. The question of how to achieve a quantitative agreement between the theoretical and experimental values by correcting the closure relation is also discussed.

I-Q-2 Molecular Theory of an Electrochemical Double Layer in a Nanoporous Carbon Supercapacitor

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[*Chem. Phys. Lett.* **378**, 638 (2003)]

We develop the replica RISM theory of electrolyte solution sorbed in a nanoporous carbon electrode. The model comprises carbon nanospheres forming a disordered network with the porosity, pores sizes and surface area fitted to carbonized polyvinylidene chloride (PVDC) material, and to activated carbon. We obtained the huge capacitance comparable to that achieved in supercapacitors, and found the higher capacitance per pores surface for carbonized PVDC material with uniform nanoporous texture than for activated carbon with micro-as well as nanopores. Unlike a planar electrochemical double layer with the voltage dominated by the inner layer, the nanoporous supercapacitor voltage is driven by the solvation chemical potentials of the sorbed ions.

I-R Multicritical Behavior of Charge-Transfer Complexes

In the mixed-stack organic charge-transfer complex, TTF-CA, neutral-ionic and dimerization-induced ferroelectric phase transitions are observed. At ambient pressure, they occur simultaneously and discontinuously. Under high pressure, these transitions take place at different temperatures, that is, its phase diagram contains a paraelectric ionic phase in addition to the ferroelectric ionic and neutral phases. To treat both the ionicity (*i.e.*, degree of charge transfer from the donor to acceptor molecules) and the dimerization, which causes a finite polarization, we employ a classical spin-1 model called Blume-Emery-Griffiths model. However, this model itself cannot reproduce the proper solid-liquid-gas phase diagram due to hidden symmetries, so that an additional interaction is necessary.

I-R-1 Ferroelectric Phase Transition, Ionicity Condensation, and Multicriticality in Charge-Transfer Organic Complexes

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[*Phys. Rev. B* submitted]

To elucidate a novel pressure-temperature phase diagram of the quasi-one-dimensional mixed-stack charge-transfer (CT) complex TTF-CA, we study the quasi-one-dimensional spin-1 Blume-Emery-Griffiths (BEG) model. In addition to the local charge transfer energy and the inter-stack polar (dipole-dipole) interaction, we take account of the inter-stack electrostriction effect. Using the self-consistent chain-mean-field theory, where the intra-stack degrees of freedom are exactly treated by the transfer-matrix method, we reproduce the gas-liquid-solid like phase diagram corresponding to the neutral (N), paraelectric ionic (I_{para}), and ferroelectric ionic (I_{ferro}) phases, respectively. We also give an explanation on the experimentally observed multicritical behavior and concomitant discontinuous inter-stack lattice contraction in TTF-CA.

I-S Photoinduced Phase Transitions in Charge-Transfer, Spin-Crossover, and Binuclear Metal Complexes

Now a variety of materials show photoinduced phase transitions. Their characters depend much on the magnitude of the hysteresis loop. The TTF-CA complex has small hysteresis and the transition is described by a deterministic approach. Especially, macroscopic coherent oscillations of neutral-ionic domain walls need to be described by a model that consists of interacting electrons and lattice displacements. The evolution of the system is described by the time-dependent Schrödinger equation. On the other hand, organometal spin-crossover complexes generally have large hysteresis and the transition is described by a stochastic approach. Ising-like models are sufficient to describe the slow transition between high- and low-spin phases. The evolution of the system is governed by thermal processes and described by the master equation. Even in a case with large hysteresis, a deterministic approach can be useful. In the iodine-bridged binuclear platinum complexes with ligand pop, a photoinduced transition takes place mainly from the charge-density-wave to charge-polarization phases within a large hysteresis loop. Its explanation needs off-diagonal elements of the Hamiltonian, so that a deterministic approach is necessary.

I-S-1 Electronic and Lattice Dynamics in the Photoinduced Ionic-to-Neutral Phase Transition in a One-Dimensional Extended Peierls-Hubbard Model

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Real-time dynamics of charge density and lattice displacements is studied during photoinduced ionic-to-neutral phase transitions by using a one-dimensional extended Peierls-Hubbard model with alternating potentials for the one-dimensional mixed-stack charge-transfer complex, TTF-CA. The time-dependent Schrödinger equation and the classical equation of motion are solved for the electronic and lattice parts, respectively. We show how neutral domains grow in the ionic background. As the photoexcitation becomes intense, more neutral domains are created. Above threshold intensity, the neutral phase is finally achieved. After the photoexcitation, ionic domains with wrong polarization also appear. They quickly reduce the averaged staggered lattice displacement, compared with the averaged ionicity. As the degree of initial lattice disorder increases, more solitons appear between these ionic domains with different polarizations, which obstruct the growth of neutral domains and slow down the transition.

I-S-2 Coherence Recovery and Photoinduced Phase Transitions in One-Dimensional Halogen-Bridged Binuclear Platinum Complexes

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A photoinduced transition from a charge-density-wave (CDW) phase to a charge-polarization (CP) phase has been recently found in a one-dimensional halogen-bridged binuclear platinum complex $R_4[Pt_2(pop)_4I]$-nH_2O (pop = $P_2O_5H_2^{2-}$, R = $(C_2H_5)_2NH_2$). Its mechanism is theoretically studied by solving the time-dependent Hartree-Fock equation for a one-dimensional two-band three-quarter-filled Peierls-Hubbard model. Above a threshold in the photoexcitation intensity, a transition takes place from the CDW to CP phases. The threshold intensity depends on the relative stability of these phases, which can be explained qualitatively by their diabatic potentials. However, the transition from the CP to CDW phases is hardly realized for two reasons: (i) low-energy charge-transfer processes occur only within a binuclear unit in the CP phase; (ii) it is difficult for the CDW order to become long-ranged owing to its weak coherence. The effective transfer integrals required for the coherence are evaluated.

I-S-3 Two-Step Photo-Induced Phase Transitions in a Two-Sublattice Model

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Photo-induced phase transition (PIPT) phenomena in organometal spin-crossover complexes have been widely investigated. As an effective model for a two-step spin transition, we study a two-sublattice spin model that takes into account an intra-site antiferromagnetic coupling and inter-site ferromagnetic couplings. Since each site takes low-spin (L) or high-spin (H) state, the model has four (LL, LH, HL, and HH) possible phases. First, we discuss the temperature dependence of the high spin fraction by using a mean-field approximation. The results indeed show a two-step spin transition due to the competition between the intra- and inter-site couplings. Next, we apply Monte Carlo (MC) simulations including a photoexcitation term. The MC dynamics of the high spin fraction shows non-linear characteristics such as step-like change, threshold-like behavior, and phase separation.

I-S-4 Quasiparticle Structure in the Vicinity of the Heisenberg Model: One and Higher Dimensions

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We study quasiparticle structures in a class of quantum spin and half-filled Hubbard models where the antiferromagnetic correlation is suppressed. First, we focus on the one-dimensional case and study how the solitonic quasiparticles and their bound states appear. Then, we propose its analogue in higher dimensions and compare the results with those of the two-dimensional Hubbard model at half filling on a triangular-type lattice.