RESEARCH ACTIVITIES I
Department of Theoretical Studies

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

Theories of the electronic structure of molecules have been extensively developed for last decades. There are, however, plenty of challenging and practically important problems to be solved.

I-A-1 Multireference Linear Response Theory Utilizing the State Universal Coupled Cluster Formalism

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In the multireference linear response theory (MRLRT), energy differences (excitation energies, ionization potentials, and electron affinities) including multielectron processes are calculated accurately in a size-intensive manner. The original formalism follows the generalization of the coupled cluster linear response theory (CCLRT) employing the Adamowicz-type wave operator ansatz for the state specific coupled cluster (SSCC) theory. The effective Hamiltonian is however contaminated by near-degeneracy correlation effects at far from the equilibrium geometry of the specified state. We develop a time-dependent perturbation theory which utilizes the state universal CC formalism. It is shown that the present MRLRT describes our-valence states more naturally such that they are size-intensive to all valence excited states in the complete model space.

I-A-2 Size-extensive Calculations of Static Structure Factors from the Coupled Cluster Singles and Doubles Model

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[*J. Chem. Phys.* **111**, 827 (1999)]

The X-ray incoherent scattering factor S(q), which is also called the static structure factor, is very sensitive to electron correlation. In this study a method for calculating S(q) based on coupled cluster singles and doubles (CCSD) approach is developed and the computed S(q) of H_2O, CH_3OH, CH_3CN, C_6H_6, and C_6H_{12} are compared with experimental results. It is shown that the CCSD method improves theoretical S(q) of large molecules significantly compared with those by configuration interaction singles and doubles (CISD) previously employed.

I-A-3 Local Resolution of Identity for Scalable Molecular Orbital Calculations

TEN-NO, Seiichiro; IWATA, Suehiro

The resolution of identity (RI) technique in the calculations of four-center electron repulsion integrals has been used in the density functional, HF, MCSCF, MP2, CCSD and CCSD(T) molecular orbital theories. The use of RI reduces the formal scaling of the integral calculation and storage to be only $O(n^3)$. This does not however mean that any step of the theories reduces the scaling of the calculation. To mitigate this situation, we develop a new decomposition scheme, the local resolution of identity (LRI), employing different expansion sets for different charge distributions of local basis functions. It is shown that LRI provides powerful alternatives with possibly wider applicability for computing large molecular systems.

I-A-4 On Connection Between The Reference Interaction Site Model Integral Equation Theory and The Partial Wave Expansion of The Molecular Ornstein-Zernike Equation

TEN-NO, Seiichiro; IWATA, Suehiro

[*J. Chem. Phys.* **111**, 4865 (1999)]

We develop a systematic integral equation theory based on the partial wave (PW) expansion of the Ornstein-Zernike (OZ) equation for molecular fluids. The obtained partial OZ (POZ) equation indicates that the total correlation function is a chain sum of the direct ones in the PW form joined by the “full” intra-molecular correlation functions, including angular dependency explicitly. On this basis, the site-site OZ (SSOZ) equation in the reference interaction site model (RISM) is identified as an approximation to POZ, truncated at the lowest order in the angular expansion. This fact provides us a rigorous and transparent framework to formulate integral equation theories for multiple site treatments. We also derive proper Helmholtz free energy and closure expressions based on the PW formalism.

I-A-5 Non-Adiabatic Relaxation Through a Conical Intersection

IKEGAMI, Tsutomu; IWATA, Suehiro

The non-adiabatic transition through a conical intersection is studied for a two-dimensional two-level model system. The two adiabatic potential energy surfaces are set up to be flat, except for the conical intersection located at the origin. Around the conical intersection, the upper adiabatic surface is concaved, so that the classical trajectories running on the upper surface are attracted to the intersection. Since the non-adiabatic coupling between two adiabatic surfaces diverges at the conical intersection, trajectories passing nearer to the intersection have larger probability to relax to the lower surface. Therefore, the rate of the non-adiabatic relaxation is expected to increase with the decrease of the kinetic energy. The above expectation is confirmed by both the quantum-classical mixed dynamics and the wavepacket (quantum) dynamics.

I-B Water Clusters and Their Complexes with Atomic Ions

While we have been studying water cluster anions $(H_2O)_n^-$, we have found a unique structural unit in which the OH bonds surround an excess electron. We call it OH{e}HO structure. This structure is also found in the water cluster complexes with a group 1 metal atom. The interaction between the electron and HO bonds is very similar to the hydrogen bond; in the structure OH{e}HO, the bond length of OH is lengthened and the harmonic frequency of OH stretching modes shifts substantially downward. The structure is expected to be ubiquitous, and further both theoretical and experimental studies are required.

I-B-1 Theoretical Studies of Structures and Ionization Threshold Energies of Water Cluster Complexes with a Group 1 Metal, $M(H_2O)_n$ (M = Li and Na)

TSURUSAWA, Takeshi; IWATA, Suehiro

[*J. Phys. Chem. A* **103**, 6134 (1999)]

Water cluster complexes with a group 1 metal atom, $M(H_2O)_n$ (M = Li and Na), for n = 3–6 were studied with ab initio MO methods. The singly occupied molecular orbitals (SOMO) are classified into three types; surface, quasi-valence and semi-internal. They are the isomers of structures with semi-internal SOMO that are responsible for the observed convergence of the ionization threshold energy. They are the ion-pair complexes, $M^+(H_2O)_m{\cdot}(H_2O)_{n-m-l}{\cdot}(H_2O)_l^-$, and their vertical ionization energies (VIEs) are determined by the local structure of $(H_2O)_l^-$ and the electrostatic potential from the cation $M^+(H_2O)_m$. The model also explains why the experimental ionization threshold energy converges at $n = 4$.

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

TSURUSAWA, Takeshi; IWATA, Suehiro

The stable isomers of the water cluster complexes with a group 1 metal atom can be modeled as $M(H_2O)_n = M^+(H_2O)_m{\cdot}(H_2O)_{n-m-l}{\cdot}(H_2O)_l^-$, and the similar structural unit was found as in water cluster anions. The unit consists of an localized electron distribution and the surrounding HO bonds, and we can call it the OH{e}HO structure. In the $M(H_2O)_n$, the electron is stabilized by both the OH bonds of water molecules surrounding the electron and the electrostatic potential from the hydrated metal ion part $M^+(H_2O)_m$. The interaction makes the SOMO extent measure (SEM: the volume of the sphere which contains a half of the SOMO electron) shrunken to as small as 50–60 Å^3. When the surrounding OH bonds interact with the shrunken SOMO electron in the $M(H_2O)_n$, the HO bonds are lengthened and their harmonic frequencies are shifted to low. The changes in both OH bond lengths and the harmonic frequencies are similar to those in the usual hydrogen bond. As we call the interaction in the clusters $X^-(H_2O)_n$, (X = F, Cl, Br and I) the ionic hydrogen bond, we may call the interaction between an electron and its surrounding OH bonds the electron-hydrogen bond. The electron-hydrogen bond is as strong as the ordinal hydrogen bonds, when the water molecule having the OH bond interacting with electron is a double proton acceptor. The calculations indicate that the spectral patterns in the OH stretching frequencies are well correlated with the geometric structure surrounding the electron {e}, and that the vibrational spectra help us to identify the isomers.

I-B-3 The Energies, the Structures and the Harmonic Frequencies of the Small Water Cluster Anions, $(H_2O)_n^-$ (n = 3, 4 and 6)

TSURUSAWA, Takeshi; IWATA, Suehiro

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

For the small water cluster anions $(H_2O)_n^-$ (n = 3, 4 and 6), the isomers which have the internally bound electron in the cluster have found by the ab initio MO methed. We have added four, three and two diffuse functions on all oxygen atoms for trimer, tetramer and hexamer clusters, respectively. For trimer, the obtained structure contains three fragments (each fragment is a water molecule) surrounding the excess electron and there is no bond between the fragments. For the tetramer, the isomers contain two fragments which surround the excess electron between the fragments. For hexamer anions, the structure of the isomers determined in this calculations have a ring structure. Because the SOMO extent measure (SEM) is large even in the hexemer anions (150–250 Å^3), the change of OH bond length and the change of the harmonic frequencies are not large as in the water cluster complexes containing a group 1 metal atom $M(H_2O)_n$. The excess electron in the water cluster anions are stabilized by the surrounding OH bonds and the electrostatic potential made by the dipole moment of the fragments of the cluster. Because the electrostatic potential from the dipole moment of the fragment water cluster does not make the SEM shrunken as in the $M(H_2O)_n$, the interaction between the excess electron and surrounding OH bonds are not strong. Due to the large SEM of the excess electron in the hexamer anions, those structures are not exactly the internal structures. For the hexamer, the isomers which have separate fragments surrounding the excess electron might be possible and those might have smaller SEM than the isomers determined in this calculations.

I-B-4 Theoretical Study of Vibrational Spectra for $Cl^-(H_2O)$: Temperature Dependence and the Influence of Ar_n (n = 1–3)

SATOH, Katsuhiko; IWATA, Suehiro

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

Vibrational spectra for $Cl^-(H_2O)$ in the OH stretching region were studied theoretically. The theoretical results are compared with the experimental results from two groups. They are in closer agreement with one of the reported spectra. By adiabatically separating the intermolecular and intramolecualar modes, the potential surfaces for the intermolecular modes are drawn with and without the excitation of the OH stretching mode. The contribution from the hot bands are examined by solving the 2-dimensional vibrational nuclear Schrödinger equation. The argon clusters attached to $Cl^-(H_2O)$ as a spectator contribute the substantial downward shift of the ionic hydrogen-bonded OH stretching frequency.

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

We have started a new research project, "Computational Chemistry for Atmospheric Environmental Molecule" under Research and Development Applying Advanced Computational Science and Technology administrated by Japan Science and Technology Corporation (ACT-JST). Because almost all of molecules in the atmosphere on the earth are simple molecules, we can perform the state-of-the-art calculations for the atmospheric molecules, and the calculational results are accurate enough to be used as "the experimental data" if they are not available. Physical and chemical phenomena in the atmosphere sometimes involve a sequence of complex processes. To explore the processes, development of new theoretical methods might be required.

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

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

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

Accurate calculations are performed for several doublet and quartet states of CO^+ with the multi-reference configuration interaction method using augmented quadruple zeta basis set. To calculate the transition probability among the electronic states and to draw well-balanced potential energy curves, a single set of molecular orbitals determined by Iwata's VALVAC method is used in the multi-reference single-double configuration interaction calculations. Spectroscopic constants and the lifetimes of vibronic states are calculated and compared with the available experimental data. Table 1 shows the lifetimes of the vibronic states of the $B^2\Sigma^+$ state. Experimental and theoretical results by Marian *et al.* are also shown. The calculated lifetimes of the vibronic states are in perfect agreement with the available experimental data within the experimental error. Our calculations confirm the lifetime measurement by Marian *et al.* The accuracy in our calculations is expected to hold for higher vibrational quantum numbers. It should be emphasized that the evaluation of the lifetime of the vibronic states in the B state requires the Einstein's A coefficients to the vibronic levels of both $A^2\Pi$ and $X^2\Sigma^+$ states.

Table 1. The lifetimes (in *n* sec.) of the vibronic levels of $B^2\Sigma^+$ state

$B^2\Sigma^+$ state v'	v' = 0	1	2	3	4	5
Lifetime	56.40	61.48	66.87	72.31	78.32	83.34
Marian *et al.* (exp.)	57.1 ± 1.0	61.8 ± 1.0	68.9 ± 1.0	72.5 ± 2.7		
Marian *et al.* (theo.)	50.00	54.9	59.7	64.9		

I-C-2 Accurate Potential Energy Curves of Several Electronic States of N_2^+ and O_2^+

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

Accurate calculations are performed for several doublet and quartet states of N_2^+ and O_2^+ with the multi-reference configuration interaction method using augmented quadruple zeta basis set. Spectroscopic constants are obtained and are compared with latest PFI-PE experiment. The calculated spectroscopic constants well reproduce the existing experimental data. The high ionic states, which have been detected in the low resolution photoelectron spectra as shake-up bands, are well characterized.

I-C-3 Absorption and Emission Spectra Among the Rovibrational Levels of the Electronic Ground State of CO $X^1\Sigma^+$

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

Carbon monoxide molecule is one of the important molecules in the atmosphere not only on the earth but also on the other planet. With the spectrometer on a satellite, high resolution infrared absorption spectra of solar atmosphere are reported up to high $J \geq 100$, and the data were used to determine Dunham's coefficients accurately. In this study, rovibrational levels of CO $X^1\Sigma^+$ state are calculated, and the calculated spectroscopic constants well reproduce the experimental Dunham's coefficients. By evaluating Einstein's A and B coefficients, the lifetime of each rovibrational level is estimated, and the rotational resolved IR absorption and emission spectra are simulated for $\Delta v = 2$ and 3 as well as $\Delta v = 1$ transitions.

I-C-4 Theoretical Study of the Reactions of OH Radical with Hydrocarbons

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OH radical is one of the most reactive chemical species with hydrocarbons. In this study, atmospheric chemical reactions of OH radical with some simple hydrocarbons are investigated using ab initio molecular orbital methods. Molecular geometries are optimized at the MP2/aug-cc-pVDZ level and single point energy calculations are performed at the CCSD(T)/aug-cc-pVDZ level. In the hydrogen abstraction reactions with saturated hydrocarbons such as methane and ethane, weekly-bound reactant complexes are found as the experiment suggests. Calculated binding energies of the reactant complexes are 0.74 kcal/mol for $CH_4\cdots OH$ system and 0.83 kcal/mol for $C_2H_6\cdots OH$ system. On the other hand, the product complexes have the binding energies of 1.99 kcal/mol and 3.25 kcal/mol, respectively. The reaction barrier heights are computed at 6.48 kcal/mol for $CH_4\cdots OH$ system and 3.70 kcal/mol for $C_2H_6\cdots OH$ system. Electron correlation effect has a large influence on both molecular structures and relative energies.

I-C-5 *Ab Initio* Study of the Low-Lying Excited States of ClOCl

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The photo-dissociation spectrum of ClOCl, from Nickolaisen *et al.* (*J. Chem. Phys.* **104**, 2857 (1996)), was investigated using the Multi-Reference Configuration Interaction (MRCI) method; the aug-cc-pVTZ basis set was used for all the calculations. Twelve low-lying states are examined in all 6 singlet states and 6 triplet states, which correlated to the ClO($^2\Pi$) + Cl(^{2}P). Our calculations, as well as the calculations shown by Nickolaisen *et al.*, strongly suggest that a weak and broad band at 2.3 eV cannot be assigned to OCl2, and that the next band at 2.9 eV is assigned to the transition to the triplet state 1^3B_1. The low lying excited states, both singlet and triplet, are all dissociative to ClO + Cl.

I-C-6 *Ab Initio* Study of the Excited States of HOBr

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To analyse the recently reported absorption spectrum of HOBr by Ingham *et al.* (*J. Phys. Chem. A* **102**, 3293 (1998)), CASSCF and multi-reference CI calculations were carried out with aug-cc-pVDZ basis set augmented by a set of Rydberg orbitals. The first weak band at 2.71 eV, previously not reported, is assigned to the transition to the lowest triplet state ^{3}A". Two UV bands at 3.53 and 4.37 eV are the transitions to 1^1A" and 2^1A' states, respectively. Because the triplet states are closely lying near these states, to study the photodissociaton processes after the UV irradiation, the spin-orbit coupling should be taken into account. There are several valence and Rydberg excited states between 6.5 and 8.0 eV, which contribute the absorption spectra near 200 nm.

I-C-7 Theoretical Study of the Molecular Structure of the $NO_3^-(HNO)_m$ and $NO_3^-(HNO)_m\cdot H_2O$ Anions

ENGLAND, James[1]; IWATA, Suehiro
([1]Univ. Surrey)

The molecular structure of the atmospheric NO_3^--$(HNO)_m$ and $NO_3^-(HNO)_m\cdot H_2O$ anions were studied at both the MP2 and DFT (using the B3LYP functional) levels of theory with the Gaussian 98 program. Using a 6-31++G* basis set, the geometry of the anions were optimized. The symmetric structure $[O_2NO–H–ONO_2]^-$ is not at the local minimum on the potential energy surface, and the NO_3^- plane is almost perpendicular to the plane of $HONO_2$. The calculated binding energy at the MP2 level for $NO_3^-(HNO)$ was found to be 123.37 kJ/mol, and 120.58 kJ/mol at the DFT. Work is currently underway to study the effect of water hydrogen bonding to the anion, as well as increasing m to two and eventually three.

I-C-8 Investigation of the Potential Energy Surfaces for the Ground X^1A_1 and Excited C^1B_2 Electronic states of SO_2

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[*Chem. Phys. Lett.* **303**, 441 (1999)]

The stationary points along the dissociation path are investigated by means of high-level ab initio MO methods and the reliability of different methods is discussed. The multi-reference AQCC method using the ANO-type basis set is shown to give geometrical parameters and relative energies in very good agreement with experiment. At this level of theory, the $\tilde{C}^1B_2(^1A')$ state has an asymmetrical equilibrium geometry and double-minimum potential with a barrier of 170 cm^{-1}, in good agreement with experimental data.

I-D Application of Ab Initio Molecular Orbital Methods to Experimentaly Relevant Systems

The quantum chemical calculations now are indispensable tools for analyzing the experimental data and for planning new experiments. We have been collaborating with many experimental groups. Some of them have attained enough experience and started their own calculations. The close collaborative works are, yet, continuing.

I-D-1 Theoretical Study on Spectroscopic Properties of Positive, Neutral, and Negative Species of BCl_2 and $AlCl_2$: The Stability of the Negative Species

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

Accurate and predictive values of the bond lengths and angles, dipole moments, and vibrational frequencies of $BCl_2^+(X^1\Sigma_g^+)$, $BCl_2(\tilde{X}^2A_1)$, and $BCl_2^-(\tilde{X}^1A_1, \tilde{a}^3B_1)$ and the corresponding aluminum analogs are calculated by Becke's three parameter density-functiona1-theory (B3LYP) method with the augmented correlation consistent triple- and quadruple-zeta (aug-cc-pVTZ and aug-cc-pVQZ, respectively) basis sets. The coupled-cluster singles, doubles, and noniterative triples (CCSD(T)) method with aug-cc-pVTZ is also used to augment the B3LYP results. The ionization energies and electron affinities are also calculated by the B3LYP/aug-cc-pV5Z method at the B3LYP/aug-cc-pVQZ geometry and the CCSD(T)/aug-cc-PVQZ method at the CCSD(T)/aug-cc-pVTZ geometry, as well as by the G1, G2, CBS-4, and CBS-Q methods. It is shown that the negatively charged species, which have never been studied experimentally, are stable both in singlet and triplet spin states with electron affinities of l.40 eV/0.25 eV and 2.37 eV/0.46 eV for singlet/triplet states of BCl_2^- and $AlCl_2^-$, respectively. The photoelectron spectra for the electron detachment of the anions are simulated by calculating the Franck-Condon factors. The photoelectron spectra for the singlet and triplet states of BCl_2^- turn out to be very similar to $AlCl_2^-$ analogs. While the photoelectron spectra for $\tilde{X}^2A_1(MC1_2) \leftarrow \tilde{X}^1A_1(MCl_2^-)$, M = B and Al, have complicated combination bands, those for $\tilde{X}^2A_1(MCl_2) \leftarrow \tilde{a}^3B_1(MCl_2)$, M = B and Al, have only one vibrational progression of the symmetric stretch mode.

I-D-2 The Structures of the Ground and Excited States of (H_3NHNH_3) Radical

CHEN, Feiwu[1]; OKADA, Kazutoshi[2]; IWATA, Suehiro
([1]JST; [2]GUAS)

The potential energy surface of the cation $(H_3NHNH_3)^+$ ground state was calculated by MP2 with aug-cc-pVTZ basis set, and the surface was fitted to an analytical function by Levenberg-Marquardt method. The potential energy curves of the neutral (H_3NHNH_3) ground state and first three excited states were calculated with UHF-CIS with the same basis set as for the cation. It can be seen from those curves that the barrier for proton transfer becomes lower and the tunneling effect, especially for the first excited state, becomes significant when the distance between two nitrogen nuclei is smaller. The bond length of the cation calculated by MP2 is 2.697 Å, which is in excellent agreement with the experiment data 2.69(5) Å, while the bond length calculated by HF is a little larger, 2.822 Å. These data show the importance of the correlation effect in the computation. The frequencies for the cation and the neutral's first excited state are also calculated to attempt analyzing the recently reported absorption spectrum of (H_3NHNH_3) radical.

I-D-3 The Heat of Formation of the SiF_2^{++} Dication: A Theoretical Prediction

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[*Int. J. Mass Spectrom.* in press]

The energetics of the SiF_2^{++} dication and of its related fragments were calculated using different ab initio MO method, including the semiempirically corrected G2, the complete basis set (CBS) method, and the coupled cluster method up to the CCSD(T)/aug-cc-pVQZ level. The individual values of bond energies and ionization potentials were carefully compared to the available experimental data in order to get an insight into the accuracy of these approaches. In addition, reaction enthalpies for the possible fragmentation reactions were calculated. All these calculations allow a reliable prediction of the heat of formation of the SiF_2^{++} dication of 546 ± 2 kcal/mo1.

I-D-4 Electronic Isomers in $[(CO_2)_nROH]^-$ Cluster Anions. II. *Ab initio* Calculations

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

Ab initio MO calculations have been performed for the $[(CO_2)_nROH]^-$ (R = H and CH_3) anions with $n = 1$ and 2. Three stable structures are found for $[(CO_2)H_2O]^-$, and two structures for $[(CO_2)CH_3OH]^-$. All the $[(CO_2)ROH]^-$ structures are characterized by the charge localization on the CO_2 moiety, which interacts with ROH through an O–H···O linkage. It is also revealed that the addition of ROH to CO_2^- leads to the formation of a potential barrier against autodetachment higher than that of a bare CO_2^-, which results in the increasing stability of $[(CO_2)ROH]^-$ species. For $n = 2$ the calculations predict the existence of two types of isomers having different degrees of the excess electron localization: $CO_2^- \cdot CO_2(ROH)$ and $C_2O_4^- \cdot ROH$ isomers. These “electronic isomers” are calculated to be close in energy, while their calculated vertical detachment energies (VDEs) differ by more than 1 eV. The *ab initio* results are discussed in comparison with recent experimental ones derived from photoelectron spectra of $[(CO_2)_nROH]^-$.

I-D-5 Theoretical Studies of $[Si_4NO]^-$ Clusters with *Ab Initio* MO and DFT Methods

WANG, Wen-Ning[1]; TANG, Hai-Rong[1]; FAN, Kang-Nian[1]; IWATA, Suehiro
([1]Fudan Univ.)

[*Chem. Phys. Lett.* **310**, 313 (1999)]

Various isomers of $[Si_4NO]^-$ cluster have been studied at both UHF/6-31G* and UB3LYP/6-31G* levels. The optimized structures and harmonic vibrational frequencies were calculated at both levels of approximations. Two obviously different groups of isomers have been found as in the case of $[Si_4NO]^+$, and the Si_4^- cluster shows higher reactivity toward NO molecule than Si_4^+. The differences between anionic and cationic Si_4NO clusters and the comparison with the experimental results were discussed.

I-D-6 Theoretical Studies of Core-Excitation and Auger-Decay Processes in Site- or State-Specific Bond Dissociation Reaction with *Ab Initio* MO Methods

MITANI, Masaki[1]; TAKAHASHI, Osamu[1]; SAITO, Ko[1]; IWATA, Suehiro
([1]Hiroshima Univ.)

In several recent experiments using soft X-ray light source, molecules having CO and CN groups separated by a CH_2 chain, such as CH_3OCOCH_2CN and $CH_3CO(CH_2)_3CN$, indicate the site- or state-specific bond dissociation after photo-excitation of core electron. These reactions suggest the possibility of controlling chemical reaction by inner shell excitation by selectively breaking a chemical bond at a desired atomic site. Thus, to predict the selective chemical processes, it is important to theoretically explore the reaction mechanisms of core-excitation, Auger-decay and bond-dissociation processes.

Photo-absorption spectrum is calculated by the static exchange (STEX) approximation as follows: (i) electronic structure calculations of ground and core-holed states, (ii) construction of STEX Hamiltonian and (iii) imaging of spectrum. STEX procedure is applied to $CH_3OCO(CH_2)_nCN$ ($n = 0$–3) using DZP+Rydberg and TZP+Rydberg basis sets with 20s20p20d functions on the core-holed atom. The comparison between theoretical and experimental results for CH_3OCOCH_2CN indicates that the former basis set is too small for quantitative estimation of peak positions in both N- and O-edge spectra. Two peaks assigned to N(1s) → π*(CN) and N(1s) → π*(CO), respectively, have been observed by N-edge experiment around 400 eV. If N and CO are separated by a CH_2 unit, however, the direct excitation N(1s) → π*(CO) has no transition moment. Therefore, only one peak, which corresponds to the N(1s) → π*(CN) excitation, is found in the STEX calculations. On the other hand, in the experimental spectra there are two peaks found. The theoretical N(1s) → π*(CN) peak for the enol-isomer of this molecule is shifted by about 0.4 eV from that of the keto-isomer. It is most probable that one of experimental peaks is the band of the enol structure.

Auger transition rates from core-holed molecules are estimated by means of Mulliken population analysis. Because the exact calculation of Auger intensity is difficult for molecular systems, approximated procedures may be desired. Transition probability in Auger decay process is expressed by the integrals including unknown Auger electron orbital, and such calculations have been performed only for diatomic molecules. As for polyatomic molecules, the estimation is carried out frequently by employing the integrals for isolated atoms. If the contribution of Auger electron is omitted, Auger intensity correlates with the orbital overlap between initial core-holed and final valence-holed orbitals. Since core molecular orbital (MO) is localized on specific atom, it is expected that the intensity may be approximated by Mulliken populations of valence-holed MOs at core-holed site. Auger final state is two-hole state, and we examine three-types of approximation as sum, product and square of two valence MO populations. These methods are applied to simple molecules of H_2O, CO, H_2CO, C_2H_2, C_2H_6, CH_3CN, CF_3CN with cc-pVDZ basis functions. MO populations are calculated from Hartree-Fock MO for neutral molecules. These approximations seems to be able to use for qualitative analysis of experimental normal Auger spectrum. Further refinement with the CI wave function for two-hole final states are now in progress.

I-E 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-E-1 Classification of Low-Energy Conformations of Met-Enkephalin in the Gas Phase and in a Model Solvent Based on the Extended Scaled Particle Theory

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([1]GUAS; [2]Kyushu Inst. Tech.)

[*Bull. Chem. Soc. Jpn.* **72**, 1717 (1999)]

We employed Monte Carlo simulated annealing method to classify the low-energy conformations of Met-enkephalin in the gas phase and in aqueous solution. In order to include the free energy of cavity formation in aqueous solution, we used the method of extended scaled particle theory. This was the first attempt to combine the Monte Carlo simulated annealing method and the extended scaled particle theory. We conducted 20 Monte Carlo simulated annealing runs of 10000 Monte Carlo sweeps both in the gas phase and in aqueous solution. It was found that the obtained conformations (20 each) can be classified into 3 groups of similar structure both in the gas phase and in aqueous solution. We studied in detail the structural characteristics of the classified conformations. It was found that the cavity-formation effects of aqueous solution do not drastically change the backbone structures obtained in the gas phase. The relation between the solvent-accessible surface area and the cavity-formation free energy was studied in detail. The results show unambiguously that the cavity-formation free energy is not necessarily proportional to the accessible surface area, at least for a small peptide.

I-E-2 Temperature Dependence of Distributions of Conformations of a Small Peptide

MITSUTAKE, Ayori[1]; HANSMANN, Ulrich H. E.[2]; OKAMOTO, Yuko
([1]GUAS; [2]Michigan Tech. Univ.)

[*J. Mol. Graphics Modell.* **16** (1999) in press]

We have performed a multicanonical Monte Carlo simulation of Met-enkephalin in order to study its low-energy conformations in detail. The obtained conformations are classified into six groups of similar structures by the pattern of intrachain hydrogen bonds. We have identified six such groups. Several thermodynamic quantities such as the distributions of hydrogen bonds and those of backbone dihedral angles are obtained as a function of temperature. From these results, it was concluded that at least four of the six groups are well-defined local-minimum-energy states.

I-E-3 α-Helix Propensities of Homo-Oligomers in Aqueous Solution Studied by Multicanonical Algorithm

MITSUTAKE, Ayori[1]; OKAMOTO, Yuko
([1]GUAS)

[*Chem. Phys. Lett.* **309**, 95 (1999)]

Helix-coil transitions of homo-oligomers in aqueous solution are studied by multicanonical Monte Carlo simulations. The solvation effects are represented by the term that is proportional to the solvent-accessible surface area of the peptides. Homo-oligomers of length 10 are considered for two characteristic amino acids, alanine and glycine, which are helix former and helix breaker, respectively. It is shown that the helix-coil transition temperature for homo-alanine in water is considerably lower than in gas phase. The helix propagation parameter s and nucleation parameter σ for both alanine and glycine are calculated and shown to be in remarkable agreement with experimental results.

I-E-4 Replica-Exchange Molecular Dynamics Method for Protein Folding

SUGITA, Yuji; OKAMOTO, Yuko

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

We have developed a formulation for molecular dynamics algorithm for the replica-exchange method. The effectiveness of the method for protein folding problem is tested with a penta peptide, Met-enkephalin. The method can overcome the multiple-minima problem by exchanging non-interacting replicas of the system at several temperatures. From only one simulation run, one can obtain probability distributions in canonical ensemble for a wide temperature range by the multiple-histogram reweighting techniques, which allows the calculation of any thermodynamic quantity as a function of temperature in that range.

I-F Theoretical Studies of Chemical Reaction Dynamics

I-F-1 Quantum Reaction Dynamics of Heavy-Light-Heavy Systems: Reduction of the Number of Potential Curves and Transitions at Avoided Crossings

NOBUSADA, Katsuyuki[1]; TOLSTIKHIN, Oleg I.[2]; NAKAMURA, Hiroki
([1]Hokkaido Univ.; [2]IMS and Lebedev Phys. Inst.)

[*J. Phys. Chem. A* **102**, 9445 (1998)]

Two decoupling procedures are proposed within the framework of the hyperspherical coordinate approach in order to reduce the number of states in the close-coupling calculations and to clarify the reaction mechanisms. Sharply avoided adiabatic states are diabatically connected and relabeled without any diabatic coupling there. This is named diabatic decoupling and is useful for decoupling two manifolds of states belonging to different categories. Furthermore, the number of states is reduced in such a way that only a limited number of adjacent adiabatic states are taken into account in the close-coupling calculations for each relevant state. This is called adiabatic decoupling scheme. These reductions of the number of states enable us to analyze reactions in terms of nonadiabatic transitions at avoided crossings among the small number of adiabatic potential curves. The method is applied to O(^{3}P) + HCl → OH + Cl and Cl + HCl → HCl + Cl. The idea of vibrationally nonadiabatic transitions at avoided crossings together with the concept of potential ridge introduced in our previous paper can untangle the congested potential curves and clarify reaction mechanisms.

I-F-2 Quantum Reaction Dynamics of Cl + HCl → HCl + Cl: Vibrationally Nonadiabatic Reactions

NOBUSADA, Katsuyuki[1]; TOLSTIKHIN, Oleg I.[2]; NAKAMURA, Hiroki
([1]Hokkaido Univ.; [2]IMS and Lebedev Phys. Inst.)

[*J. Mol. Struct. (THEOCHEM)* **461-462**, 137 (1999)]

Quantum reaction dynamics of Cl + HCl → HCl + Cl for J (total angular momentum) = 0 is studied with use of the hyperspherical *elliptic* coordinate approach recently proposed by the authors. Thanks to the numerical efficiency of this approach, the reactions involving vibrational quantum jumps up to three are calculated accurately. Actually, all transitions among the states up to $v = 3$ and $j = 15$, in other words up to the total energy $E = 1.3$ eV, are covered, where v and J represent vibrational and rotational quantum numbers, respectively. Because of the symmetry of the system, the vibrationally adiabatic reactions are generally more probable than the nonadiabatic ones. However, some specific vibrationally nonadiabatic reactions even with two or three vibrational quantum jumps are found to occur efficiently. The concepts of potential ridge and non-adiabatic transitions at avoided crossings near the ridge lines enable us to comprehend the reaction mechanisms nicely.

I-F-3 Quantum Reaction Dynamics of an Asymmetric Exoergic Heavy-Light-Heavy System: Cl + HBr → HCl + Br

MIL'NIKOV, Gennady V.[1]; TOLSTIKHIN, Oleg I.[2]; NOBUSADA, Katsuyuki[3]; NAKAMURA, Hiroki
([1]IMS and Inst. Struct. Macrokinetics, Russia; [2]IMS and Lebedev Phys. Inst.; [3]Hokkaido Univ)

[*Phys. Chem. Chem. Phys.* **1**, 1159 (1999)]

Quantum dynamics calculations for HBr + Cl → Br + HCl are carried out using the hyperspherical elliptic coordinates. The concepts of potential ridge and nonadiabatic transitions at avoided crossings introduced previously for isoergic and symmetric three-dimensional heavy-light-heavy reactions are confirmed to be useful to clarify the mechanisms of vibrationally non-adiabatic reactions in this exo-(or endo-)ergic system. The role of important avoided crossings which dominate the reaction dynamics is illustrated.

I-F-4 On the *J*-Shift Approximation in Quantum Reaction Dynamics

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

[*J. Phys. Chem. A* **103**, 6715 (1999)]

The validity of the J-shift or the energy-shift approximation is investigated numerically by taking the reaction O(^{3}P) + HCl → OH + Cl as an example. The approximation based only on the results of J (total angular momentum quantum number) = 0, which is the ordinary J-shift approximation, cannot reproduce the exact reaction dynamics well, especially when the initial rotational quantum number is high. The reaction rate constants for specified initial rovibrational states are over- or underestimated depending on the initial state and temperature. The good agreement with the accurate result of the thermal rate constant seems to be rather accidental because of the cancellations of these over- and underestimates. An extended J-shift approximation is proposed, in which accurate calculations should be carried out up to $J = j_i$ with $|\Omega| \leq \Omega_{\max}$ when $j_i \leq \Omega_{\max}$, or up to $J = \Omega_{\max}$ when $j_i > \Omega_{\max}$, where $\Omega_{\max}$ is the maximum of the absolute values of the body-fixed projection quantum number Ω that give noticeable contributions to the reaction dynamics. When the maximum J required to have a well converged cross-section and rate constant is much larger than j_i it is recommended to carry out accurate calculations at some representative J values and to use these values to estimate probabilities at other J values by an appropriate interpolation or extrapolation procedure.

I-F-5 Electronically Adiabatic Chemical Reactions Analyzed by the Semiclassical Theory of Nonadiabatic Transition

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

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

I-G Theory of Nonadiabatic Transition

I-G-1 Patterns of Time Propagation on the Grid of Potential Curves

OSTROVSKY, Valentin N.[1]**; NAKAMURA, Hiroki**
([1]Inst. Phys., Univ. St. Petersburg, Russia)

[*Phys. Rev. A* **58**, 4293 (1998)]

Time-propagation patterns are studied for a network formed by two bands of equidistant rectilinear parallel diabatic potential curves that cross each other. In the case of weak coupling between the bands the propagation proceeds mostly via a diabatic path. In the case of strong coupling a different regime of anti-diabatic propagation is revealed. For the intermediate case of coupling strength the propagation is basically described by an overlay of diabatic and antidiabatic patterns; interestingly, the adiabatic propagation is never operative. The present dynamic quantum model is compared with those models that assume a reduction of the problem to a succession of pairwise transitions between the states.

I-G-2 Analytic Solution of Two-State Time-Independent Coupled Schrödinger Equations in an Exponential Model

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

[*Phys. Rev. A* **59**, 2486 (1999)]

Quantum mechanically exact analytical solutions are obtained for a two-state exponential model, in which the exponent of diabatic coupling is one-half of that of the diabatic potential curve. A very simple and accurate semiclassical formula is found for the nonadiabatic transition probability.This gives a direct generalization of the Landau-Zener and Rosen-Zener formulas.

I-G-3 Semiclassical Theory of Nonadiabatic Transitions in a Two-State Exponential Model

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

The two-state exponential model (repulsive potential case) is investigated and the two channel scattering problem is solved by means of semiclassical theory and high energy approximation. The analytical expression for the nonadiabatic transition matrix agrees with the previous attractive case. The only variables in this formula are the model-independent adiabatic momenta contour integrals. Oscillations of the overall transition probability when the energy is below the crossing of diabatic potentials can be observed in the case of large coupling. Unified theory of nonadiabatic transitions, covering the Landau-Zener-Stueckelberg and Rozen-Zener-Demkov models, is the aim of the present study.

I-H New Way of Controlling Molecular Processes

I-H-1 New Way of Controlling Molecular Processes by Time-Dependent External Fields

TERANISHI, Yoshiaki[1]**; NAKAMURA, Hiroki**
([1]GUAS)

[*J. Chem. Phys.* **111**, 1415 (1998)]

A new idea of controlling molecular processes by time-dependent external fields is proposed. Molecular processes in external fields are considered to be composed of a sequence of time-dependent nonadiabatic transitions in which the external fields play a role of adiabatic parameters. Unit final transition probability can be achieved with the use of the interference effects among various paths created by nonadiabatic transitions. The basic idea is to sweep the external field periodically at each avoided crossing and to control the transition there completely as we desire. This idea is quite general, and can hold whatever the external field is. Various control schemes can be proposed corresponding to the various types of time-dependent nonadiabatic transitions. The methods of π-pulse and chirped laser pulse with the adiabatic rapid passage may be considered as special cases of the present idea. As an example, a one-dimensional model of the laser-induced ring-puckering isomerization of trimethylenimine is considered, and comparative studies on the effectiveness and the stability of the various control schemes proposed in this paper are made together with presentation of numerical examples.

I-H-2 Control of Molecular Photodissociation with Use of the Complete Reflection Phenomenon

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

In the one-dimensional nonadiabatic tunneling type curve crossing, there always occurs the intriguing phenomenon of complete reflection at certain discrete energies. We may think of controlling molecular processes with use of this phenomenon by applying a strong static laser field. By dressing up the electronic ground state of a molecule and adjusting the laser frequency appropriately, we can create the nonadiabatic tunneling potential surface crossing and the complete reflection condition to stop the dissociation into a certain direction. Although the complete reflection cannot be "complete" in a multi-dimensional space, we can control molecular photodissociation to some extent. Even in the case that a molecule cannot dissociate into a certain direction because of a high potential barrier in the excited state, we can dissociate that molecule into such a channel with use of the present method in principle. Two-dimensional model systems mimicking HOD and CH_3SH molecules are numerically studied.

I-I Molecular Switching with Use of the Complete Reflection Phenomenon

I-I-1 Molecular Switching in a Two-Dimensional Constriction

NAKAMURA, Hiroki

[*J. Chem. Phys.* **110**, 10253 (1999)]

The new idea of molecular switching discussed previously for the one-dimensional system [Nanbu, Nakamura and Goodman; *J. Chem. Phys.* **107**, 5445 (l997)] is extended to a two-dimensional constriction model. Analytical formulation is provided with use of the Mathieu functions and the semiclassical theory of nonadiabatic transition. Numerical demonstrations are also carried out. Both reflection and transmission, and thus the switching cannot be complete like in the one-dimensional case, but the switching is demonstrated to be quite effective. Although this is a purely theoretical model at this stage, some practical implications are discussed.

I-J Theoretical Study of Dissociative Recombination

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

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

[*Comput. Phys. Commun.* in press]

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

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

I-K-1 The Fifth- and Seventh-Order Two-Dimensional Raman Spectroscopy for Harmonic System with Nonlinear System-Bath Interactions: Gaussian-White Case

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

The quantum Fokker-Planck equation is derived for a system that is nonlinearly coupled to a harmonic heat bath. The interaction between the two subsystems is assumed to be linear in the bath coordinate but quadratic in the system coordinate. The relaxation-induced dynamics of the system are investigated by simulating the third-, fifth-, and seventh-order Raman response of a harmonic mode. The Wigner phase space representation of the wave packet dynamics provides useful insight in the nonlinear character of the system-bath coupling. For weak system-bath coupling the third-order Raman response can be explained by the perturbation theory of Okumura and Tanimura, which predicts a line width linear proportional to temperature. When the two subsystems interact strongly, the first-order perturbation theory breaks down. The impulsive fifth- order Raman response shows that in addition to the frequency fluctuations induced by the bath higher-order energy transfer between system and bath has to be considered. The nonlinearity of the system-bath interaction yields also an interesting feature in the impulsive seventh-order Raman echo response: The calculations predict a finite signal for the case of a harmonic potential and a linear coordinate dependence of the polarizability while for linear system-bath coupling this response vanishes completely due to destructive interference of different Liouville space pathways.

I-K-2 The Fifth and Seventh Order 2D Raman Spectroscopy for Harmonic System with Nonlinear System-Bath Interactions: Gaussian-Markovian Case

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

A potential system nonlinnealy coupled to a Gaussian-Markovian heat bath is considered. The interaction between the two subsystems is assumed to be linear in the bath coordinate but quadratic in the system coordinate. This model delivers the frequency modulation of the potential and can be regarded as a half-breed of a Brownian oscillator model and stochastic two-level model. We deduce the quantum Fokker-Planck equation for a Gaussian-Markovian noise bath for this nonlinear system-bath interaction in the hierarchy form. An inhomogeneous broadening of molecules, which was traditionally modeled by the overdamped limit of a stochastic two-level system, is studied for a harmonic potential system by numerically integrating the equation of motion. The third-, fifth- and seventh-order off-resonant Raman signal, which are expressed by the two-, three-, and four-time correlation function of polarizability, respectively, are calculated as the subject of two-dimensional Raman spectroscopy. Theses signals are very different from the result of a Brownian oscillator case. Raman echo peaks, which were predicted from the stochastic two-level theory, are observed in the two-dimensional seventh-order signal. It was shown that the seventh-order two- dimensional Raman spectroscopy is useful to measure the inhomogeneity of liquids, in the case where the fifth-order 2D signals were very weak.

I-K-3 Structural Information from Two-Dimensional Fifth-Order Raman Spectroscopy

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

[*J. Chem. Phys.* **111**, 492 (1999)]

Two-dimensional (2-D) fifth-order Raman spectroscopy is a coherent spectroscopy that can be used as a structural tool, in a manner analogous to 2-D nuclear magnetic resonance (NMR) but with much faster time scale. By including the effect of dipole-induced dipole interactions in the molecular polarizability, it is shown that 2-D Raman experiments can be used to extract distances between coupled dipoles, and thus elucidate structural information on a molecular level. The amplitude of cross peaks in the 2-D Raman spectrum arising from dipole-induced dipole interactions is related to the distance between the two dipoles (r) and the relative orientation of the dipoles. In an isotropic sample with randomly distributed dipole orientations, such as a liquid, the cross peak amplitude scales as r^6 In an anisotropic sample such as a solid, where the orientational averaging effects do not nullify the leading order contribution, the amplitude scales as r^3. These scaling relationships have analogy to the dipole coupling relationships that are observed in solid state and liquid 2-D NMR measurements.

I-K-4 Two-Dimensional Line Shape Analysis of Photon Echo Signal

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

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

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

I-K-5 Cage Dynamics in the Third-Order Off-Resonant Response of Liquid Molecules: A Theoretical Realization

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

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

I-K-6 Dynamical Stokes Shift Observed by Two-Dimensional Raman Spectroscopy

SUZUKI, Yoko; TANIMURA, Yoshitaka

We analyze the effect of relaxation process of wavepackets created in the electronic excited state on off-resonant two-dimensional Raman spectroscopy, employing the Brownian motion model with a non-equilibrium initial condition described by a displaced Gaussian wavepacket. We calculate three-time correlation functions of the excited state polarizability, which correspond to the fifth-order Raman signal in the excited state by using the Feynman's path integral formalism. It is found that the fifth-order signal is sensitive to the initial position of the Gaussian wavepacket not only for the underdamped case but also for the overdamped case.

I-K-7 A Thermal Bath Induced New Resonance in Linear and Nonlinear Spectra of Two-Level Systems

GANGOPADHAYAY, Gautam[1]; GHOSHAL, Sharmistha[1]; TANIMURA, Yoshitaka
(*[1]S. N. Bose Natl. Cent. Basic Sci.)*

[*Chem. Phys.* **242**, 367 (1999)]

Within the scope of generalized master equation we have shown the effect of bath with finite bandwidth on the linear absorption and on the resonance fluorescence and absorption spectra of a driven two-state system. It is found that depending on the bandwidth and temperature of the bath a reversible dynamics may set in even in the case of linear absorption induced by weak field. At higher temperature the bath induces new resonance on the spectral profiles.

I-L Ab Initio Molecular Orbital Studies of Organic Conductors

I-L-1 Structures and Electronic Phases of the Bis(Ethylenedithio)Tetrathiafulvalene (BEDT-TTF) Clusters and κ-(BEDT-TTF) Salts: A Theoretical Study Based on Ab Initio Molecular Orbital Methods

IMAMURA, Yutaka[1]; TEN-NO, Seiichiro; YONEMITSU, Kenji; TANIMURA, Yoshitaka
(*[1]GUAS)*

[*J. Chem. Phys.* **111**, 5986 (1999)]

Electronic and geometrical structures of bis-(ethylenedithio)tetrathiafulvalene (BEDT-TTF) molecules are studied using ab initio molecular orbital methods. The optimized structure of a BEDT-TTF monomer is close to the experimental one within errors of 0.02 Å and 0.5 degree in bond length and angle, respectively, except the ethylene group. Ab initio parameters such as transfer integrals and Coulomb interactions are determined from the BEDT-TTF dimer and tetramer calculations. Using model Hamiltonians with the ab initio parameters, we investigate the electronic states based on the exact diagonalization method. The results show that the ground state has antiferromagnetic correlation which is consistent with experimental results. We study the effects of long-range Coulomb interactions employing the 2-D extended Hubbard model with the Hartree-Fock approximation. It is found that the ground state shows various phases; antiferromagnetic, charge ordering, and paramagnetic ones, controlled by the long-range interactions.

I-L-2 Ab Initio MO Studies on Electronic States of DCNQI Molecules

IMAMURA, Yutaka[1]; TEN-NO, Seiichiro; TANIMURA, Yoshitaka
(*[1]GUAS)*

[*J. Phys. Chem. B* **103**, 266 (1999)]

Electronic and geometrical structures of DR-DCNQI molecules (R = H, Cl, Br, I, Me and OMe) were studied by performing ab initio MO calculations at the HF/DZP level. We carried out DCNQI monomer calculations and found that the optimized structures are close to experimental ones within errors of 0.04 Å in a six-membered ring. We then discussed the basis set dependence of geometrical parameters and concluded that the polarization functions improve the description for double and triple bond states. Ab initio parameters such as transfer integrals were calculated for DCNQI dimers and trimers and compared with formerly calculated parameters. We found that the transfer integrals correlate well with lattice parameters of the c axis.

I-L-3 Theoretical Study on Electron Correlation of 1-D (DCNQI)$_2$M (M = Li, Ag)

IMAMURA, Yutaka[1]; TEN-NO, Seiichiro; YONEMITSU, Kenji; TANIMURA, Yoshitaka
([1]GUAS)

[*Chem. Phys. Lett.* **298**, 15 (1998)]

We study electronic states of the (DCNQI)$_2$M (M = Li and Ag) salts based on the full configuration interaction (FCI) method using effective Hamiltonians derived from the ab initio molecular orbital theory. FCI results of the DCNQI tetramer and octamer models indicate that the ground state has the antiferromagnetic and charge ordering correlations. It corresponds to the 2 kF spin density wave and 4 kF charge density wave states (SDW and CDW). In the octamer model, it is also found that some low-lying excited states have similar spin-flipped CDW correlations and the antiferromagnetic correlation is weakened.Electronic and geometrical structures of DR-DCNQI molecules (R = H, Cl, Br, I, Me and OMe) were studied by performing ab initio MO calculations at the HF/DZP level. We carried out DCNQI monomer calculations and found that the optimized structures are close to experimental ones within errors of 0.04 Å in a six-membered ring. We then discussed the basis set dependence of geometrical parameters and concluded that the polarization functions improve the description for double and triple bond states. Ab initio parameters such as transfer integrals were calculated for DCNQI dimers and trimers and compared with formerly calculated parameters. We found that the transfer integrals correlate well with lattice parameters of the *c* axis.

I-M Electron, Poritron and Heavy Particle Scattering Dynamics

We are concerned with theoretical aspects on scattering dynamics resulting from electron, positron, and ion and atom collisions with polyatomic molecules. A few subjects we put emphasize are: (i) a comparative study of electron and positron scattering from polyatomic molecules, (ii) dissociative positron attachment, (iii) resonances in electron, positron and ion impacts on molecules, and (iv) atomic collisions at ultra-low temperature.

I-M-1 Strong Mode Dependence of 3.8-eV Resonance in CO_2 Vibrational Excitation by Electron Impact

KIMURA, Mineo[1]; TANAKA, Hiroshi[2]; KITAJIMA, Masashi[2]; TAKEKAWA, Michiya[3]; ITIKAWA, Yukikazu[3]
([1]Yamaguchi Univ. and IMS; [2]Sophia Univ.; [3]Inst. Space Astro. Sci.)

Vibrational excitation modes are significantly enhanced by the presence of the shape resonance at 3.8 eV in a CO_2 molecule, but these modes are found to show quite different energy-dependence in the resonance peak. This feature arises from the different interaction scheme for excitation to each mode, *i.e.*, the weak polarization interaction for excitation to the symmetric stretching mode, weak dipole interaction for excitation to the bending mode, and strong dipole interaction for excitation to the asymmetric stretching mode. The asymmetric stretching shows sharp increase in differential cross sections (DCSs) toward small angle scattering due to the strong dipole interaction which washes out resonance features appeared at intermediate angles. DCSs for the symmetric and bending modes clearly show conspicuous isotropic features around 3.8 eV, thus emerging a sharp resonance.

I-M-2 Strong Suppresion of Positronium Formation in Fluorinated Hydrocarbons in Positron Scattering: A Possibility of Bound States

SUEOKA, Osamu[1]; KIMURA, Mineo[1,2]
([1]Yamaguchi Univ.; [2]IMS)

Strong suppression in positronium (Ps) formation is observed, for the first time, in fluorinated hydrocarbons. The reduction in Ps-formation cross sections is significantly pronounced, and the Ps-formation cross sections for fluorinated hydrocarbons (CF_4, C_2F_6, C_3F_8) are smaller by a factor of four-to-five than those for hydrocarbon counterparts (CH_4, C_2H_6, C_3H_8). This finding is a strong indication for the existence of bound states in fluorinated hydrocarbons because the high electronegativity of F atoms form F- ions, and this in turn attracts positrons and forms a bound state near the edge of the charge distribution, thus reducing Ps formation.

I-M-3 Electron Capture in Collisions of Protons with CO Molecules in the keV Region: The Steric Effect

KIMURA, Mineo[1]; GU, Jian-ping[2]; HIRSCH, Gerhard[2]; BUENKER, Robert J.[2]; STANCIL, P. C.[3]
([1]Yamaguchi Univ. and IMS; [2]Bergische Univ.; [3]Oak Ridge Natl. Lab.)

Electron capture resulting from collisions of H^+ ions with CO molecules has been investigated based on the molecular representation within the fully quantum mechanical formalism below 10 keV/u. Three different molecular configurations have been considered for collision dynamics, *i.e.*, (i) the proton approaches the center of mass of the CO molecule in the perpendicular configuration, (ii) the proton approaches the C atom in the collinear configuration, and (iii) the proton approaches the O atom in the collinear configuration. Electron capture dynamics and corresponding capture cross sections depend very sensitively on the molecular configuration, thus revealing a strong steric effect. The capture cross section from the CO electronic ground state is about 1.3×10^{-15} cm^2 at 10 keV/u, which is in good agreement with experimental findings. Differential cross sections (DCS's) for three molecular orientations have been examined both for elastic and electron capture processes, and the DCS averaged over all the configurations was found to agree well with a measurement from 0.02° to 1° at 1.5 keV/u.

I-M-4 The Isomer Effect on Charge Transfer: Collisions of Ground State C^+ Ions with Allene and Propyne (C_3H_4)

KIMURA, Mineo[1]; KUSAKABE, Toshio[2]; IMOU, Kazumichi[2]; SATOH, Shinichi[2]; NAKANISHI, Hiroshi[2]; TOMITA, Noriaki[2]; TAWARA, Hiroyuki[3]; NAKAI, Yohta[2]
([1]Yamaguchi Univ. and IMS; [2]Kinki Univ.; [3]Natl. Inst. Fusion Sci.)

The isomer effect on charge transfer in collisions of C^+ ions with allene and propyne (C_3H_4) molecules has been observed for the first time experimentally in the collision energy from 0.15 keV to 4.5 keV. In the present experiment, the ground state C^+ (^2P) ion projectiles have been produced by carefully energy-controlled electron impact to minimize the influence of the metastable-state ions. The observed cross sections are found that charge transfer cross sections for allene are slightly larger than those of propyne below 1 keV, although the difference becomes smaller as the collision energy increases. Both cross sections gradually decrease from around 1×10^{-14} cm^2 to 3×10^{-15} cm^2 as the collision energy increases from 0.2 keV to 4 keV. Since the molecular size of both molecules is similar, the size effect does not influence strongly on the cross section, but electronic structure is expected to be responsible to this difference. The dipole moment of propyne is larger by a factor of four than that of allene, which should cause the more pronounced effect on the dynamics at much lower collision energies.

I-M-5 Electron Capture and Excitation in Collisions of Si^{2+} Ions with He Atoms at Intermediate Energies

KIMURA, Mineo[1]; **SUZUKI, Satoshi**[2]; **SHIMAKURA, Noriyuki**[2]; **GU, Jian-ping**[3]; **HIRSCH, Gerhart**[3]; **BUENKER, Robert J.**[3]; **STANCIL, P. C.**[4]
([1]Yamaguchi Univ. and IMS; [2]Niigata Univ.; [3]Bergische Univ.; [4]Oak Ridge Natl. Lab.)

We have investigated electron capture and excitation in collisions of Si^{2+} ions with He atoms in the collision energy range from 0.02 keV/u to 6 keV/u based on a molecular representation. Molecular states are determined by using the multireference single- and double excitation configuration interaction method. We have considered electron capture and excitation both by the ground singlet and metastable triplet Si^{2+} ions. The capture cross section by the ground singlet Si^{2+} ion increases with increasing collision energy, and reaches a value of ~ 1.3×10^{-16} cm^2, while that by the metastable triplet ion is found to be large with a magnitude of 4×10^{-16} cm^2 at the highest energy studied. Weak, but conspicuous, oscillatory structures are found for both cases, which are due to multichannel interference. The present rate coefficient for the ground singlet Si^{2+} ion impact is found to be much smaller than those of the [Si^{4+} + He] system earlier studied

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 $g_{j\lambda}(r)$ can be calculated from the extended RISM equation. Using V_λ the solvated Fock operator is defined as,

$$F^s = F^g - \sum_\lambda \mathrm{V}_\lambda \mathrm{b}_\lambda$$

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 The Syn-/Anti- Conformational Equilibrium of Acetic Acid in Water Studied by the RISM-SCF/MCSCF Method

SATO, Hirofumi; HIRATA, Fumio

[*J. Mol. Struct. (THEOCHEM)* **461**, 113 (1999)]

The syn-/anti- conformational equilibrium of acetic acid in water is studied by the RISM-SCF/MCSCF method, a hybridized method of the *ab initio* quantum chemistry and the statistical mechanics of molecular liquids. The solvent effect on the two conformers is examined in terms of the solvation free energy. Significant stabilization due to solvation was observed on the anti-conformer, while only slight decrease in the free energy is resulted in the syn-conformer. Due to the greater stabilization in the anti-conformer, the energy gap between the two conformers is dramatically reduced in solution; 1.7 kcal /mol in solution compared with 6.9 kcal/mol in gas phase. The change in the electron density of acetic acid upon transferring the solute from gas phase into aqueous solution is visualized to understand the polarization effects due to solvent.

I-N-2 RISM-SCF Study for the Free Energy Profile of Menshutkin Type Reaction $NH_3 + CH_3Cl \rightarrow NH_3CH_3^+ + Cl^-$ in Aqueous Solution

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([1]Kyoto Univ.)

[*Theor. Chem. Acc.* **102**, 165 (1999)]

The free energy profile for the Menshutkin type reaction $NH_3 + CH_3Cl \rightarrow NH_3CH_3^+ + Cl^-$ in aqueous solution is studied using the RISM-SCF method. The effect of electron correlation on the free energy profile is estimated by the RISM-MP2 method at the HF optimized geometries along the reaction coordinate. The vibrational frequencies at the reactant, transition state and product are found to undergo a large influence by the solvation and these are utilized to calculate the zero-point energy correction of the free energy profile. The computed barrier height and reaction exothermicity are in reasonably agreement with those of the experiment and the previous calculations. The change of solvation structure along the reaction path are represented by the radial distribution functions between the solute-solvent atomic sites. The mechanisms of the reaction are discussed from the view points of solute electronic and solvation structures.

I-N-3 Thermodynamic Analysis of the Solvent Effect on Tautomerization of Acetylacetone: An Ab Initio Approach

ISHIDA, Tateki[1]; HIRATA, Fumio; KATO, Shigeki[1]
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[*J. Chem. Phys.* **110**, 3938 (1999)]

The keto-enol tautomerism of acetylacetone in solution is studied with the reference interaction site model self-consistent-field (RISM-SCF) method. We choose three solvents, H_2O, dimethyl sulfoxide (DMSO), and carbon tetrachloride (CCl_4), representing, respectively, protic polar, aprotic polar and nonpolar solvents. The analysis is made taking account of the solute electronic as well as geometrical change of the tautomers due to solvent effect. In addition, the electronic correlation energy of solute molecule and solute vibrational energies are considered. The free energy differences are analyzed by decomposing them into the enthalpy and entropy terms. The theory reproduces the total free energy determined by the experiment fairly well. We also find that, as solvent polarities increase, the keto tautomer shows the drastic geometric change in order to make its dipole moment larger and that the geometric change of the keto tautomer is enthalpically driven in H_2O and entropically in DMSO. It is made clear that these depend on the solvent property protic or aprotic.

I-N-4 Solvation Dynamics of Benzonitrile Excited State in Polar Solvents: A Time-Dependent Reference Interaction Site Model Self-Consistent Field Approach

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([1]Kyoto Univ.)

[*J. Chem. Phys.* **110**, 11423 (1999)]

The solvation dynamics of benzonitrile (C_6H_5CN) after the $2^1A_1 \leftarrow 1^1A_1$ vertical transition in water (H_2O), methanol (CH_3OH), and acetonitrile (CH_3CN) solvents is studied with the reference interaction site model self-consistent field (RISM-SCF) method. The evolution of solute electronic states associated with the solvent relaxation is described by a time-dependent RISM-SCF method, incorporating the time-dependent solute-solvent site-site radial distribution functions, which are derived from the surrogate linear response theory. Ab initio electronic structure calculations reveal that the 2^1A_1 state is of ionic nature whose dipole moment is larger by 2.41 D than that of the ground state. It is found that the excited state dipole moment is enhanced in the solutions, which provides the red shift of ~6000 cm^{-1} in the vertical excitation energy. The solvent relaxation further increases the charge polarization in solute, indicating the electronic state of excited C_6H_5CN is sensitive to the electrostatic field coming from the solvent. The dynamic Stokes shift is characterized by the solvation time correlation function (STCF). The calculated STCFs show that the solvent relaxation exhibits a nonexponential behavior and almost completes within 5 ps in H_2O and CH_3CN while a long-time tail is observed up to 20 ps in CH_3OH. The slow component of the decay rate is consistent with other simulation calculations though the fast one is smaller. In order to analyze the solute charge polarization during the solvent relaxation, the solute charge time correlation function (CTCF) is calculated and the resultant CTCFs are discussed in terms of the solvent charge polarization in the vicinity of solute molecule.

I-N-5 Revisiting the Acid-Base Equilibrium in Aqueous Solutions of Hydrogen Halides: Study by the *ab Initio* Electronic Structure Theory Combined with the Statistical Mechanics of Molecular Liquids

SATO, Hirofumi; HIRATA, Fumio

[*J. Am. Chem. Soc.* **121**, 2460 (1999)]

The classical problem of acid strength of the hydrogen halides in aqueous solution is revisited by means of the RISM-SCF/MCSCF theory, an ab initio electronic structure theory combined with the statistical mechanics of molecular liquids. Free energy changes associated with the chemical equilibrium $HX + H_2O \rightarrow X^- + H_3O^+$ are studied for a series of hydrogen halides (X: F, Cl, Br, I). The free energy differences between hydrogen halides and the dissociated anions are mainly governed by the subtle balance of the two energetic components—formation energies of hydrogen halides and solvation energies of the anions. It is shown that hydration structure around hydrogen fluoride is qualitatively different from the other three hydrogen halides. The well-known specificity of the hydrogen fluoride with respect to the acidity in aqueous solution is explained in terms of the characteristic hydration structure. Molecular geometries and electronic structures of the solute molecule as well as the solvation structure and free energy components are also discussed in detail. The old concept of electronegativity proposed by Pauling is reexamined on the basis of the modern theoretical approach.

I-N-6 Ab Initio Study on Molecular and Thermodynamic Properties of Water: A Theoretical Prediction of pK_w over a Wide Range of Temperature and Density

SATO, Hirofumi; HIRATA, Fumio

[*J. Phys. Chem. B* **103**, 6596 (1999)]

The ionic product of water (pK_w) has been calculated in a wide range of temperature (0–600 ˚C) and density (0.6–1.4 g/cm^3) by means of ab initio electronic structure theory combined with the extended reference interaction site model in statistical mechanics for molecular liquids (RISM-SCF/MCSCF). We consider the autoionization process ($H_2O + H_2O \rightarrow H_3O^+ + OH^-$) by regarding H_2O, H_3O^+ and OH^- as "solute" molecules in an aqueous solution and evaluate molecular geometries, electronic structure, solvation structure, and free energy components of these species as functions of thermodynamical conditions. The results for pK_w obtained from the theory have shown a monotonical decrease with increasing density at all the temperatures investigated, in good accord with the experimental observation. The behavior is determined essentially by the difference in solvation free energies, $\Delta\mu(H_3O^+) + \Delta\mu(OH^-) - 2\Delta\mu(H_2O)$, associated with the reaction. The $\Delta\mu(OH^-)$ shows the density dependence, which is entirely different from that of the other species and which gives rise to the observed behavior for $\Delta\log K_w$. It is shown through analyses of the electronic structure of the "solutes" that the distinct density dependence of $\Delta\mu(OH^-)$ has the origin in its rather "soft" electronic cloud interacting with solvent polarization.

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 ($V \rightarrow \infty$, $N \rightarrow \infty$, 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-O-1 Calculation of Solvation Free Energy for Peptide in Salt Solution Using the RISM Theory

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([1]Kyoto Univ.)

[*J. Comput. Chem.* **19**, 1724 (1998)]

We have developed a robust, highly efficient algorithm for solving the full reference interaction site model (RISM) equations for salt solutions near a solute molecule with many atomic sites. It is obtained as an extension of our previously reported algorithm for pure water near the solute molecule. The algorithm is a judicious hybrid of the Newton-Raphson and Picard methods. The most striking advantage is that the Jacobian matrix is just part of the input data and need not be recalculated at all. To illustrate the algorithm, we have solved the full RISM equations for a dipeptide (NH_2-$CHCH_3$-CONH-$CHCH_3$-COOH) in a 1M-NaCl solution. The extended simple point charge (SPC/E) model is employed for water molecules. Two different conformations of the dipeptide are considered. It is assumed for each conformation that the dipeptide is present either as an unionized form or as a zwitterion. The structure of the salt solution near the dipeptide and salt effects on the solvation free energy have also been discussed.

I-O-2 Singular Behavior of the RISM Theory Observed for Peptide in Salt Solution

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[*Chem. Phys. Lett.* **297**, 433 (1998)]

We examine the reference interaction site model theory applied to a peptide-salt solution system, with the assumption that a zwitterionic dipeptide (Ala-Ala) is present in NaCl solution at the infinite-dilution limit. For some sets of the parameters in the peptide-cation and peptide-anion potentials, the theory exhibits singular behavior: as the salt concentration decreases, the ionic concentration around the peptide increases and the theory eventually loses its solution. The singularity is interpreted as a signal of the ion condensation. A trend of aggregation of peptide molecules is also found.

For other sets of the potential parameters, however, no such singularity occurs. As far as the salt effects are concerned, the qualitative aspects of the conclusionsare somewhat sensitive to the potential parameters employed.

I-O-3 Analysis on Conformational Stability of C-Peptide of Ribonuclease A in Water Using the Reference Interaction Site Model Theory and Monte Carlo Simulated Annealing

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([1]Kyoto Univ.)

[*J. Chem. Phys.* **110**, 4090 (1999)]

Solvation structure and conformational stability of the C-peptide fragment of ribonuclease A in pure water, have been analyzed using the full reference interaction site model (RISM) theory. The charged groups in the side chains of Lys-1$^+$, Glu-2$^-$, Lys-7$^+$, Arg-10$^+$, and His-12$^+$ (in particular, the four like-charged groups) play substantial roles in stabilizing the conformations. The solvation free energy and the conformational energy are governed by the contribution from the electrostatic interaction with water and the intramolecular Coulombic energy, respectively, and the conformational stability is determined by competition of these two factors. The contribution from the hydrophobic hydration and the van der Waals and torsion terms in the conformational energy are less important, which is in contrast with the result for Met-enkephalin. The Monte Carlo simulated annealing combined with the RISM theory has been applied to the C-peptide using an almost fully extended conformation as the initial one. The conformation first changes in the direction that the charged groups in the side chains are more exposed to water, and in particular, the positively charged groups are closer together. Thus, the solvation free energy decreases greatly in the initial stage. Although this leads to significant increase in the intramolecular Coulombic repulsion energy, the decrease in the solvation free energy dominates. In the later stage, however, further decrease in the solvation free energy gives rise to even larger increase in the intramolecular Coulombic repulsion energy, and the conformational change is greatly decelerated. The conformations thus stabilized in four different runs of the combined program are quite similar. The peptide conformation in water is stabilized far more rapidly than in gas phase.

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 Effect of Molecular Symmetry on Electrical Potential Fluctuations of Solvent around Solute in Polar Liquid

CHONG, Song-Ho[1]; HIRATA, Fumio
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[*Chem. Phys. Lett.* **293**, 119 (1998)]

The electrical potential fluctuations of solvent around solute in polar liquid are studied using the recently developed method based on an integral equation theory of molecular liquids. We focus on how the molecular symmetry of solvent and solute affects the free energy profile governing electrical potential fluctuations of solvent around solute and characteristic parameters relevant to electron transfer reactions in solutions.

I-P-2 Mode-Coupling Theory for Molecular Liquids Based on the Interaction-Site Model

CHONG, Song-Ho[1]; HIRATA, Fumio
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[*Phys. Rev. E* **58**, 6188 (1998)]

We develop a microscopic theory for dynamics of molecular liquids which is based on the interaction-site model for polyatomic fluids, the projection-operator formalism of Zwanzig and Mori, and the mode-coupling theory. Closed nonlinear equations are derived for a self-consistent treatment of density propagation in a classical polyatomic liquid, which enable one to calculate dynamic structure factors provided the equilibrium structure functions of liquids are known.

I-P-3 Time-Correlation Functions in Molecular Liquids Studied by the Mode-Coupling Theory Based on the Interaction-Site Model

CHONG, Song-Ho[1]; HIRATA, Fumio
([1]Kyoto Univ.)

[*Phys. Rev. E* **58**, 7296 (1998)]

Numerical results for longitudinal current spectra, velocity autocorrelation functions and diffusion coefficients of a model diatomic liquid are presented using the recently developed theory for dynamics of classical polyatomic fluids. The theory is based on the interaction-site model for molecular liquids, the projection-operator formalism of Zwanzig and Mori, and the mode-coupling theory. The effect of the inclusion of the slow contribution in memory kernels, represented by the mode-coupling expression, on the aforementioned dynamical quantities is discussed. The molecular dynamics simulation of the same system is also performed to test the accuracy of our theory, and the theoretical results are found to be in fair agreement with those obtained from the simulation.

I-P-4 Dynamics of Ions in Liquid Water: An Interaction-Site-Model Description

CHONG, Song-Ho[1]; HIRATA, Fumio
([1]Kyoto Univ.)

[*J. Chem. Phys.* **111**, 3654 (1999)]

We present a molecular theory for investigating the dynamics of ions in polar liquids. The theory is based on the interaction-site model for molecular liquids and on the generalized Langevin equation combined with the mode-coupling theory. The velocity autocorrelation function, diffusion and friction coefficients of ions in water at 25 °C and at infinite dilution are studied. The theoretical results for the velocity autocorrelation functions exhibit a gradual change from oscillatory to monotonic decay as the ion size increases. The diffusion (friction) coefficients of ions in aqueous solutions pass through a maximum (minimum) as a function of the ion size, with distinct curves and maxima (minima) for positive and negative ions. These trends are in complete accord with those of the molecular dynamics simulation results performed on the same system by Rasaiah and co-workers [*J. Phys. Chem. B* **102**, 4193 (1998)]. It is worthwhile to mention that this is the first molecular theory that is capable of describing the difference in the dynamics of positive and negative ions in aqueous solutions. A further analysis of the friction coefficients of ions in water is presented in which the friction is decomposed into the “Stokes,” dielectric and their cross terms. The Stokes and dielectric terms arise from the coupling of the ion dynamics to essentially the acoustic dynamics of the solvent via the short-range interaction, and from the coupling to the optical mode of the solvent via the long-range interaction. The most striking feature of our results is that the Stokes friction so defined does not increase monotonically with increasing ion size, but decreases when ions are very small, implying a formation of a molecular “complex” comprising the ion and its nearest neighbor solvent molecules. Interesting observations concerning the cross term are: (1) its magnitude is rather large for small ions and cannot be neglected at all, and (2) the cross term for small ions seems to cancel out the Stokes part, and consequently the total friction for small ions seems to be to a large extent determined by its dielectric component.

I-P-5 Interaction-Site-Model Description of Collective Excitations in Liquid Water. I: Theoretical Study

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([1]Kyoto Univ.)

[*J. Chem. Phys.* **111**, 3083 (1999)]

Collective excitations in liquid water are investigated using the recently developed theory for dynamics of molecular liquids which is based on the interaction-site model for polyatomic fluids, the projection-operator formalism of Zwanzig and Mori, and the simple approximation scheme for memory functions. It is shown that all the essential features of collective excitations in water, reported previously by neutron-scattering experiments, molecular dynamics simulations and dielectric theories, are well reproduced by the present theory.

I-P-6 Interaction-Site-Model Description of Collective Excitations in Liquid Water. II: Comparison with Simulation Results

CHONG, Song-Ho[1]; HIRATA, Fumio
([1]Kyoto Univ.)

[*J. Chem. Phys.* **111**, 3095 (1999)]

Theoretical results for dynamical correlation functions characterizing collective excitations in liquid water reported in a previous paper are compared with molecular dynamics simulation results performed on the same system. We also examine the validity and accuracy of the approximation scheme for memory functions employed in our theory by investigating whether the assumed form for memory functions and resulting expressions for dynamical correlation functions can be used as faithful models to reproduce the "experimental" data determined from the simulation.

I-P-7 Solvation Dynamics of a Quadrupolar Solute in Dipolar Liquids

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[*J. Phys. Soc. Jpn.* **68**, 303 (1999)]

A microscopic calculation of solvation dynamics of dipolar and quadrupolar solutes in liquid water and acetonitrile is presented. The solvation is found to be biphasic. The calculated solvation time correlation function of ionic quadrupolar solute (K^+) in water is in good agreement with recent computer simulation results. Present study reveals some interesting aspects of quadrupolar solvation dynamics which differ significantly from that of ionic and dipolar solvation.

I-P-8 Density Matrix for an Excess Electron in a Classical Fluid: Results for a One-Dimensional System

SETHIA, Ashok; HIRATA, Fumio; SINGH, Yashwant[1]
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[*J. Chem. Phys.* **110**, 10086 (1999)]

We extend the theory of Chandler, Singh, and Richardson [*J. Chem. Phys.* **81**, 1975 (1984)] to calculate the density matrix for an excess electron in a classical liquid like bath. For a one-dimensional fluid of hard rods and for two model potentials representing the electron fluid atom interaction (one representing the excluded volume effect and the other attractive interaction), we calculate the density matrix using the values of solvent induced potential surfaces for the electron found from our earlier calculations [*Phys. Rev. B* **42**, 6090 (1990)]. The resulting density matrix is diagonalized and values of energies and wave-functions of the electron including the effective mass and root mean square (RMS) displacement R_β in imaginary time $\beta h/2\pi$. The transition of the electron to a state of self-trapping is visualized through a sudden change in the value of R_β or the effective mass m^* at a value of β or solvent density ρ^*. For a potential model of hard rods, we find that the RMS displacement R_β for a given solvent density varies as $(\beta h/2\pi)^\nu$. Values of ν are evaluated for several solvent densities.

I-P-9 Polaron Density Matrix and Effective Mass at Finite Temperature

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[*Phys. Rev. B* **60**, 7245 (1999)]

We calculate the density matrix elements of the polaron using the Feynman's variational method. The density matrix is diagonalized and the eigenvalues and eigenfunctions are derived. These results and the calculated density matrix are used to evaluate the root mean square (RMS) displacements R_β and the effective mass (EM) m^* for various vaues of coupling strengths between electron and medium and the temperature. We find that EM is related to the RMS displacement. The temperature dependence of EM is in qualitative agreement with experiment.

I-Q Liquid-Solid Interface

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

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

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

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I-Q-1 Acceleration of Liquid Structure Calculations by Modified Direct Inversion in the Iterative Subspace

KOVALENKO, Andriy F.; TEN-NO, Seiichiro; HIRATA, Fumio

[*J. Comput. Chem.* **20**, 928 (1998)]

We proposed a modified procedure of the direct inversion in the iterative subspace (DIIS) method to accelerate convergence in the integral equation theory of liquids. We update the DIIS basis vectors at each iterative step by using the approximate residual obtained in the DIIS extrapolation. The procedure is tested by solving the three-dimensional (3D) generalization of the reference interaction site model (RISM) equation together with the hypernetted chain (HNC) closure as well as their one-dimensional version. We calculated the 3D site distribution of water, represented by the simple point charge (SPC) model, around one water molecule considered as a central particle.

I-Q-2 Extended States of a Shallow Donor Located Near a Semiconductor-Insulator Interface

KOVALENKO, Andriy F.

[*Int. J. Quantum Chem.* **66**, 435 (1998)]

Scattering of a conduction electron by a charged shallow donor located near a semiconductor-insulator interface in the semiconductor or by a charged center embedded in the insulator is considered within the model of a hydrogen-like atom in a semi-infinite space. The interface influence is allowed for by spatial confinement of the electron envelope wavefunction. The impurity electrostatic image at the interface is taken into account. The problem is separable in prolate spheroidal coordinates and thus is solvable exactly. A rapidly convergent expansion is proposed for the angular eigenfunctions. The radial eigenfunctions are calculated directly by numerical integration of the radial boundary value problem. Expansions of the scattering wavefunction and the scattering amplitude in terms of the eigenfunctions of the problem are obtained. Using the extended and localized state wavefunctions, the photoionization cross-section of a shallow donor near a semiconductor-insulator interface is calculated. It is presented as a superposition of the oscillator strengths of transitions to the partial extended eigenstates that constitute the scattering wavefunction. Near the interface, the cross-section is enhanced significantly and redistributed over the direction of photoionized electron escape. The photoionization threshold follows the localized state energy varying with the donor - interface distance.

I-Q-3 Free Energy Profiles of Electron Transfer at Water-Electrode Interface Studied by the Reference Interaction Site Model Theory

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[*Chem. Phys. Lett.* **305**, 251 (1999)]

Free energy profiles governing electron transfer from a reactant to an electrode surface in water are investigated, based on the reference interaction site model (RISM) theory. Three models of a redox pair for charge separation reactions are examined: a pair of atomic solutes, and systems consisting of an atom and a surface with a localized or a delocalized electron. The profile becomes highly asymmetrical, when an electron in the electrode is delocalized. The behaviors are essentially due to the asymmetrical response of water polarization to positive and negative charges of solute. The results are related to models of ion-hydration.

I-Q-4 Self-Consistent Description of a Metal-Water Interface by the Kohn-Sham Density Functional Theory and the Three-Dimensional Reference Interaction Site Model

KOVALENKO, Andriy F.; HIRATA, Fumio

[*J. Chem. Phys.* **110**, 10095 (1999)]

We have developed a self-consistent description of an interface between a metal and a molecular liquid by combination of the density functional theory in the Kohn-Sham formulation (KS DFT) for the electronic structure, and the three-dimensional generalization of the reference interaction site model (3D RISM) for the classical site distribution profiles of liquid. The electron and classical subsystems are coupled in the mean field approximation. The procedure takes account of many-body effects of dense fluid on the metal-liquid interactions by averaging the pseudopotentials of liquid molecules over the classical distributions of the liquid. The proposed approach is substantially less time-consuming as compared to a Car-Parrinello-type simulation since it replaces molecular dynamics with the integral equation theory of molecular liquids. The calculation has been performed for pure water at normal conditions in contact with the (100) face cubic centered (fcc) surface of a metal roughly modeled after copper. The results are in good agreement with the Car-Parrinello simulation for the same metal model. The shift of the Fermi level due to the presence of water conforms with experiment. The electron distribution near an adsorbed water molecule is affected by dense water, and so the metal-water attraction follows the shapes of the metal effective electrostatic potential. For the metal model employed, it is strongest at the hollow site adsorption positions, and water molecules are adsorbed mainly at the hollow and bridge site positions rather than over metal atoms. Layering of water molecules near the metal surface is found. In the first hydration layer, adsorbed water molecules are oriented in parallel to the surface or tilted with hydrogens mainly outwards the metal. This orientation at the potential of zero charge agrees with experiment.

I-Q-5 Effective Interaction between Hard Sphere Colloidal Particles in a Polymerizing Yukawa Solvent

GEE, Richard H.[1]**; HENDERSON, Douglas**[2]**; KOVALENKO, Andriy F.**
([1]Snow College; [2]Brigham Young Univ.)

[*J. Chem. Phys.* **110**, 8189 (1999)]

The effective interaction between colloidal hard sphere particles in a Yukawa solvent that can polymerize with the formation of chains and rings is studied and compared with the corresponding results for colloidal hard sphere particles in a solvent of polymerizing hard spheres. The attractive nature of the polymerizing Yukawa solvent particles induces significant changes in the effective interactions between the colloid particles as compared to a polymerizing solvent of hard spheres that was investigated in previous studies. The results for the colloid-solvent mixture are obtained using the associative Percus-Yevick approximation for Wertheim’s Ornstein-Zernike integral equation; the colloidal species are taken at a non-vanishing but very small concentration throughout this article. We present the effects of the size ratio of colloid spheres to solvent spheres, the degree of polymerization, and the solvent density on the effective interactions between colloid and solvent particles. The intercolloidal potential of mean force (PMF) is found to be highly dependent on these parameters for Wertheim's model. It is found that the correlations between colloid particles obtained using the Yukawa solvent model are longer ranged and more attractive than those found using the hard sphere solvent model. A greater depletion of the solvent density around the colloidal particles is also observed for the Yukawa solvent model as compared to the hard sphere model; an increased polymer chain length also enhances the depletion of the solvent density. The PMF is found to be oscillatory in structure. The oscillatory structure also depends upon the average polymer chain length, specifically, the oscillatory structure in the PMF is strongly diminished as the average polymer chain length increases. Additionally, as the average polymer length increases, the attraction at the colloid-colloid contact distance decreases.

I-Q-6 Potential of Mean Force between Two Molecular Ions in a Polar Molecular Solvent: A Study by the Three-Dimensional Reference Interaction Site Model

KOVALENKO, Andriy F.; HIRATA, Fumio

[*J. Phys. Chem. B* **103**, 7942 (1999)]

The orientationally dependent potential of mean force (PMF) between two charged polyatomic solutes immersed in a polar molecular solvent is obtained by using the three-dimensional reference interaction site model (3D RISM) of the integral equation theory. We propose the partially linearized hypernetted chain (PLHNC) closure. The method is applied to the *N*,*N*-dimethylaniline cation (DMA^+) and the anthracene anion ($AN^–$) in acetonitrile solvent (CH_3CN). We solve the 3D RISM integral equations by employing the modified direct inversion in the iterative subspace (MDIIS) method. The 3D site distributions of solvent around each solute are obtained and discussed. The PMF between the solutes is calculated as a 3D profile dependent on the relative position of the solutes at six characteristic relative orientations. The PMF obtained is in qualitative agreement with the results of molecular dynamics simulations. In solvent, the $AN^–$ solute effectively attracts the DMA^+ dimethylamino group and repels its phenyl ring. We found that the most stable relative arrangement of the DMA^+ and $AN^–$ molecules in acetonitrile solvent is different from that in gas phase.

I-Q-7 Self-Consistent, Kohn-Sham DFT and Three-Dimensional RISM Description of a Metal-Molecular Liquid Interface

KOVALENKO, Andriy F.; HIRATA, Fumio

[*J. Mol. Liq.* submitted]

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

I-R Dimensional Crossovers and Randomness Effects in Quasi-One-Dimensional Organic Conductors

Electronic states in pure one dimension and those in two or three dimensions are very different from each other. In many organic conductors and copper oxides, applying external or chemical pressure controls dimensionality. The induced dimensional crossovers are classified by what kind of transverse coherence is restored by increasing dimensionality, i.e., one-particle coherence or two-particle coherence. Which coherence is restored depends on the asymptotic property of the corresponding one-dimensional system. The Tomonaga-Luttinger liquid is known to be unstable against interchain hopping since the transverse one-particle coherence is easily restored. In other one-dimensional phases, however, the transverse one-particle process is strongly suppressed by electron correlation, and then the transverse two-particle coherence is relatively easily restored. In the quasi-one-dimensional organic conductor, $(TMTTF)_2X$, the charge gap suppresses the transverse one-particle coherence and the two-particle crossover is accompanied by the antiferromagnetic transition. The details are investigated by the perturbative renormalization-group method from high to low temperatures and by the density-matrix renormalization-group method for the ground states. We also study the effects of random potential scattering on the competition among the Mott insulator, the Anderson localization, and the Fermi liquid phases, all of which are realized in $(DI\text{-}DCNQI)_2Ag_{1\text{-}x}Cu_x$ and $(DMe\text{-}DCNQI)_2Li_{1\text{-}x}Cu_x$.

I-R-1 Spin-Density-Wave Phase Transitions in Quasi-One-Dimensional Dimerized Quarter-Filled Organic Conductors

KISHINE, Jun-ichiro; YONEMITSU, Kenji

[*J. Phys. Soc. Jpn.* **68**, 2790 (1999)]

We have studied spin density wave (SDW) phase transitions in dimerized quarter-filled Hubbard chains weakly coupled via interchain one-particle hopping, t_{b0}. It is shown that there exists a critical value of t_{b0}, t_b^*, between the incoherent metal regime ($t_{b0} < t_b^*$) and the Fermi liquid regime ($t_{b0} > t_b^*$) in the metallic phase above the SDW transition temperature. By using the 2-loop perturbative renormalization-group approach together with the random-phase-approximation, we propose a SDW phase diagram covering both of the regimes. The SDW phase transition from the incoherent metal phase for $t_{b0} < t_b^*$ is caused by growth of the intrachain electron-electron umklapp scattering toward low temperatures, which is regarded as pre-formation of the Mott gap. We discuss relevance of the present result to the SDW phase transitions in the quasi-one-dimensional dimerized quarter-filled organic conductors, $(TMTTF)_2X$ and $(TMTSF)_2X$.

I-R-2 Phase Transitions from Incoherent and from Coherent Metal Phases in Quasi-One-Dimensional Organic Conductors

KISHINE, Jun-ichiro; YONEMITSU, Kenji

[*J. Low Temp. Phys.* in press]

We study effects of a preformed Mott gap and dimensionality on interchain one-particle coherence and spin-density-wave phase transitions in weakly coupled, dimerized quarter-filled Hubbard chains. A phase diagram is given, based on the two-loop perturbative renormalization-group (RG) approach together with the random phase approximation. Feedback effects of inter-chain processes on the umklapp process are examined by the 1 + ε expansion. We discuss relevance of the present result to the SDW phase transitions in the quasi-one-dimensional dimerized quarter-filled organic conductors, $(TMTTF)_2X$ and $(TMTSF)_2X$.

I-R-3 Quantum Phase Transition and Collapse of Mott Gap in $d = 1 + \varepsilon$ Dimensional Half-Filled Hubbard Systems

KISHINE, Jun-ichiro

[*Recent Prog. Many-Body Theories* **3** submitted]

A correlation-induced charge gap (Mott gap) plays the key role on physical properties of low-dimensional strongly correlated electron systems such as organic conductors or high-T_c cuprate superconductors. In this paper, we study dimensionality effects on the gap in $d = 1 + \varepsilon$ continuous dimension, where $0 < \varepsilon \ll 1$. By solving the one-loop renormalization-group equations, we found a quantum phase transition at a critical dimension, d_c, which depends on the strength of the Hubbard repulsion, U. For $d < d_c$, the Mott gap opens at the fixed point, $g_{3;\infty} = -G_\infty = \infty$, while for $d > d_c$, the Mott gap collapses at the fixed point, $g_{3;\infty} = const.$, $G_\infty = 0$. This result indicates that the Mott gap decreases with raising dimensionality.

I-R-4 Charge Gap and Interchain Correlation in Quasi-One-Dimensional Dimerized Organic Conductors

YONEMITSU, Kenji

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

We study the relation between the charge gap and the interchain one-body correlation function in quasi-one-dimensional dimerized organic conductors at quarter filling, by applying the density matrix renormalization group method to a three-chain extended Hubbard model. The charge gap increases with the degree of dimerization in the intrachain hopping integrals. When the charge gap is larger than the inter-chain hopping integral, the interchain hopping correlation is strongly suppressed, as observed in the $(TMTTF)_2X$ salts.

I-R-5 Magnetic and Pairing Correlation Functions and Interchain Coherence in Quasi-One-Dimensional Dimerized Organic Conductors

YONEMITSU, Kenji

[*J. Low Temp. Phys.* in press]

We study how magnetic and pairing correlation evolves with an increasing interchain hopping integral and decreasing dimerization of intrachain hopping integrals, by applying the density matrix renormalization group (DMRG) method to a three-chain extended Hubbard model at quarter filling for quasi-one-dimensional organic conductors, $(TMTTF)_2X$ and $(TMTSF)_2X$. Magnetic correlation changes from weakly coupled chains of large-amplitude spin density waves to an interchain-coherence-developed spin density wave. Pairing correlation increases, though it still decays exponentially owing to a charge gap for parameters considered here.

I-R-6 Effects of Dimerization on Spin, Charge and Hopping Correlation Functions in Quasi-One-Dimensional Organic Conductors

YONEMITSU, Kenji

[*Physica B* in press]

In order to see the effects of dimerization, interchain hopping, and nearest-neighbor repulsion on various one- and two-body correlation functions in quasi-one-dimensional organic conductors, $(TMTTF)_2X$ and $(TMTSF)_2X$, we apply the density matrix renormalization group method to a three-chain extended Hubbard model at quarter filling. The hopping correlation function shows that the interchain one-particle coherence is strongly suppressed when a charge gap due to the dimerization is larger than the interchain hopping integral. Meanwhile, the spin-spin and charge-charge correlation functions show that the interchain particle-hole coherence is rather insensitive. The charge-charge correlation function is more sensitive to the nearest-neighbor repulsion than the charge gap.

I-R-7 Interplay of Correlation, Randomness and Dimensionality Effects in Weakly-Coupled Half-Filled Random Hubbard Chains

KISHINE, Jun-ichiro; YONEMITSU, Kenji

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

We study interplay of electronic correlation, randomness and dimensionality effects in half-filled random Hubbard chains weakly coupled via an interchain one-particle hopping. Based on the two-loop renormalization-group approach, phase diagrams are given in terms of temperature *vs.* strengths of the intra-chain electron-electron umklapp scattering, the random scattering and the interchain one-particle hopping. For strong umklapp scattering and weak interchain hopping, the antiferromagnetic phase is replaced by the Anderson localization phase with increasing random scattering. For weak umklapp scattering and strong random scattering, the Anderson localization phase is replaced by the Fermi liquid phase with increasing interchain hopping. For strong umklapp scattering and weak random scattering, the antiferromagnetic phase is replaced by the Fermi liquid phase with increasing interchain hopping.

I-R-8 Dimensionality Effects in Half-Filled Random Hubbard Chains

KISHINE, Jun-ichiro; YONEMITSU, Kenji

[*Physica B* in press]

We discuss interplay of randomness, electron correlation and dimensionality effects in half-filled random Hubbard chains. Low-temperature phases are given based on the two-loop renormalization group (RG) analysis. Feedback effects of interchain processes on the umklapp process are examined by the $1 + \varepsilon$ expansion. We comment on relevance of the present result to a phase diagram of a doped organic compound, $(DI\text{-}DCNQI)_2Ag_{1-x}Cu_x$.

I-S Competition among Different Charge and Lattice Ordering States in One-Dimensional Metal Complexes

The quasi-one-dimensional halogen-bridged binuclear metal complexes (MMX chains) have strong electron-lattice coupling and electron-electron interaction. They have various electronic phases. Recently, a metallic phase has been found for the ligand dta. Meanwhile, for the ligand pop, a new insulator phase is experimentally suggested in addition to the charge density wave phase. Generally considered, possible electronic phases are i) an averaged-valence (AV) state, ii) a charge-density-wave (CDW) state, iii) a charge-polarization (CP) state, iv) an alternate-charge-polarization (ACP) state, and v) a bond-charge-density-wave state. To understand the competition among these electronic states, we need to include the on-site, two kinds of nearest-neighbor, and next-nearest-neighbor repulsion strengths between electrons in M *d* orbitals, as well as two types of electron-lattice couplings. To reproduce both of the electronic phases for the ligand dta and those for the ligand pop, we need two types of elastic couplings among M and X ions. Thus we have several parameters to control the electronic phases. So far, changing these parameters qualitatively reproduces general tendency for the dependence of the electronic state on the interdimer distance. However, the low-temperature phase of $Pt_2(dta)_4I$ has the crystal structure of the ACP phase and considerably large spin susceptibility, which remain mysterious and need further investigations.

I-S-1 Numerical Studies of Ground State Phase Diagrams for the MMX Chains

KUWABARA, Makoto; YONEMITSU, Kenji

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

We study ground state phase diagrams for the MMX chains, using a one-dimensional dimerized 3/4-filled extended Hubbard-Peierls model with site diagonal and off-diagonal electron-lattice interactions. The ground states are obtained mainly in the Hartree-Fock approximation, and their accuracy is checked by the exact diagonalization of small clusters. We find a new phase in addition to frequently considered phases and compare our results with experimental results. Without electron-electron interactions, the charge-density-wave, alternate-charge-polarization (ACP), and bond-charge-density-wave (BCDW) phases are realized depending on the electron-lattice interactions. As the site off-diagonal electron-lattice interaction increases, the ACP phase becomes stable. As the site diagonal electron-lattice interaction increases, the BCDW phase becomes stable. The on-site repulsion stabilizes the averaged-valence and charge-polarization phases, while the nearest-neighbor and next-nearest-neighbor repulsion destabilizes them.

I-S-2 Magnetic Property of MMX Chains as Dimerized Quarter-Filled Systems

KUWABARA, Makoto; YONEMITSU, Kenji

[*Physica B* in press]

We study ground state phase diagrams for the MMX chains, using a one-dimensional dimerized 3/4-filled extended Hubbard-Peierls model with site diagonal and off-diagonal electron-lattice interactions. The ground states are obtained both in the Hartree-Fock approximation and by the exact diagonalization. It has been experimentally shown that the electronic structure of $Pt_2(CH_3\text{-}CS_2)_4I$ is the alternate-charge-polarization (ACP) phase below 80K and has large magnetic susceptibility at low temperatures. Our results show the ACP phase is stable, if the site off-diagonal electron-lattice interaction, α, is strong enough, for any set of electron-electron interaction strengths. This phase is analogous to the spin-Peierls state. The spin gap is reduced as α becomes small because the lattice distortion becomes weak and the alternation of exchange interactions decreases. A possibility for the large magnetic susceptibility is that the ACP state is realized in the vicinity of the averaged-valence (AV) or charge-polarization (CP) phase. The boundary between the ACP phase and the AV or CP phase is sensitive to the interdimer-nearest-neighbor repulsion.

I-S-3 Structural and Magnetic Transitions in Quasi-One-Dimensional Halogen-Bridged Binuclear Metal Complexes

KUWABARA, Makoto; YONEMITSU, Kenji

[*Mol. Cryst. Liq. Cryst.* submitted]

We investigate ground state phase diagrams for the MMX chains, using a one-dimensional dimerized 3/4-filled extended Hubbard-Peierls model with site diagonal (α) and off-diagonal (β) electron-lattice interactions. Possible electronic states include an averaged-valence (AV) state, a charge-density-wave (CDW) state, a charge-polarization (CP) state, and an alternate-charge-polarization (ACP) state. The ground state can be controlled by choosing the metal (M), bridging halogen (X), ligand, and counter ion. The variation of X affects the model parameters, α, β, the interdimer transfer through X (t_{MXM}), the elastic constant between M and X (K_{MX}) and the interdimer repulsion strengths. As to the competition between the CDW and CP states, the boundary between them shifts upward as K_{MX} increases, and is almost independent of t_{MXM}. These results suggest the possibility of the phase control by changing the halogen ion. The CP state is characterized by coexistence of lattice distortion and gapless spin excitations. Therefore the structural transition between CDW and CP states is accompanied with a magnetic transition.

I-S-4 Electric-Field Response of Exciton in Electroluminescent Polymer

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([1]Fudan Univ.; [2]Natl. Lab. Infrared Phys.)

[*Phys. Status Solidi B* **214**, 337 (1999)]

In electroluminescent polymers, the exciton is polarized by a weak electric field *E* and dissociated by strong *E*. These effects can quantitatively elucidate the observed dependence of the luminous intensity of the luminescent polymer on the electric field and the field-induced charge generation in conjugated polymers.

I-T Transport and Magnetic Properties of Two-Dimensional Metal-Complex, Organic and Oxide Conductors

Antiferromagnetism and superconductivity are realized in two-dimensional, strongly correlated, organic materials. In κ-(BEDT-TTF)$_2$X with the quarter-filled HOMO band and strong dimerization, the electronic phases are controlled by the ratio of the effective on-site repulsion strength to the bandwidth. The metal-assembled complexes, $Et_nMe_{4-n}Z[Pd(dmit)_2]_2$, has also strong dimerization. In contrast to the former organic materials, they have a rather one-dimensional LUMO band and a two-dimensional HOMO band, both of which are largely split due to the dimerization. The phase diagram is richer than that of κ-(BEDT-TTF)$_2$X in that applied pressure induces a metal or superconductor phase depending on the cation $Et_nMe_{4-n}Z$. By using a strong-coupling expansion and mapping to an effective model, we find that the electronic phases are controlled by dimensionality and frustration due to the much more complex molecular configuration than that of κ-(BEDT-TTF)$_2$X. For example, for the cation Et_2Me_2Sb, a metallic phase appears under pressure and the antiferromagnetic order is absent because the transfer integral between next-nearest-neighbor dimers are comparable to that between nearest-neighbor ones. In addition to the materials above, many other organic conductors with various degrees of dimerization have been synthesized and the mechanisms of their insulator phases are being studied. To clarify the importance of the long-range electron-electron interactions, we are going to study optical spectra as well. The importance of the long-range electron-electron interactions is clarified also in ab initio molecular orbital, Hartree-Fock, and exact diagonalization studies of (BEDT-TTF) clusters and κ-(BEDT-TTF)$_2$X. Furthermore, the important effect of umklapp scattering processes on the quasiparticle weight is studied in the two-loop renormalization-group analysis.

I-T-1 Possible Magnetic Orders and Cation Dependence of $(Et_nMe_{4-n}Z)[Pd(dmit)_2]_2$

MORI, Michiyasu; YONEMITSU, Kenji; KINO, Hiori[1]
([1]JRCAT)

[*J. Phys. Soc. Jpn.* submitted]

We study the cation dependence of the insulating phase of Pd(dmit)$_2$ salts, based on the dimerized two-band Hubbard model. By using a strong coupling expansion, we obtain an effective Heisenberg model on an anisotropic triangular lattice. Two different magnetic orders are found possible depending on interaction strengths and the energy difference between the two bands. The variation of the cation leads to the variation of the ratio of a transfer integral in one direction to one in another direction, resulting in the variation of the ratios among the magnetic interaction strengths and that of the magnetic frustration. We calculate a sublattice magnetization at zero temperature within the linear spin wave theory and find that the antiferromagnetic order is stable except for the cation Et_2Me_2Sb, where the magnetic frustration is important. Our results are consistent with the ESR measurement.

I-T-2 Role of Dimensionality in Dimerized Two-Band Systems

MORI, Michiyasu; YONEMITSU, Kenji; KINO, Hiori[1]
([1]JRCAT)

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

We have studied the ground state properties of Pd(dmit)$_2$ salts using an effective dimer model. This model describes low-energy excitations of the two-band Hubbard model and is derived by a strong coupling expansion. Substituting the cation simultaneously controls dimensionality of the Fermi surface, density-of-states singularity, and magnetic frustration in the dimer model. For the cation Me_4P, the effective Fermi surface has much better nesting property and the effective Fermi level is located in the vicinity of the van Hove singularity. For the cation Et_2Me_2Sb, the effective Fermi surface is rather isotropic and the effective Fermi level is far from the singularity. Such cation dependence implies that the salt with Me_4P (Et_2Me_2Sb) prefers an insulating (metallic) phase, which is consistent with the experiments.

I-T-3 Quasi-One-Dimensional Natures in $(Et_nMe_{4-n}Z)[Pd(dmit)_2]_2$

MORI, Michiyasu; YONEMITSU, Kenji; KINO, Hiori[1]
([1]JRCAT)

[*J. Low Temp. Phys.* in press]

We studied one of possible ground states for Pd(dmit)$_2$ salts in a dimerized two-band Hubbard model. By using a strong-coupling expansion, we obtained an effective dimer model, which has a quasi-one-dimensional Fermi surface. In the insulating phase, it leads to the Heisenberg model on an anisotropic triangular lattice. We calculated effective exchange coupling strengths within the second order perturbation theory and found that both ferromagnetic and antiferromagnetic couplings are possible. Similarities to and differences from Ni(dmit)$_2$ salts are discussed.

I-T-4 Possible Ground State Phases of Pd(dmit)$_2$ Salts

MORI, Michiyasu; YONEMITSU, Kenji; KINO, Hiori[1]
([1]JRCAT)

[*Physica B* in press]

We have studied possible ground state phases of Pd(dmit)$_2$ salts using the two-band Hubbard model. From a strong coupling expansion, an effective model is derived and used to describe low-energy excitations. It is found that mutual interactions and dimensionality of effective bands cooperatively determine the transport and magnetic properties.

I-T-5 Collective Excitations around Charge Ordering States and Coexistent States with Different Orders

MORI, Michiyasu; YONEMITSU, Kenji

[*Mol. Cryst. Liq. Cryst.* submitted]

Novel ground states have recently been studied in molecular conductors. One is the coexistence of a spin density wave (SDW) and a charge density wave (CDW) in (TMTSF)$_2$PF$_6$, which has a quasi-one-dimensional electronic state and is the quarter-filled system with dimerization. The Hartree calculation for the one-dimensional extended Hubbard model found the coexistence of SDW and CDW. It is known that not only the on-site but also the nearest-neighbor and the next-nearest-neighbor repulsive interactions are significant. Another is the charge ordering state in θ-(BEDT-TTF)$_2$MM'(SCN)$_4$, which has a rather-two-dimensional electronic state and is the quarter-filled system with dimerization. The Hartree calculation for a two-dimensional extended Hubbard model found various charge ordering states depending on the anisotropy of the transfer integrals and that of the intersite Coulomb interaction strength. In this paper, we study collective excitations around such novel ground states and clarify effects of the dimensionality, the dimerization and the intersite Coulomb interaction on the excitation spectra. First, the ground states of one- and two-dimensional extended Hubbard models are calculated in the fully unrestricted Hartree-Fock (UHF) level to confirm the former results. Next, response functions are calculated in the random phase approximation on the basis of the UHF states to obtain the qualitative features of optical and magnetic excitations. Owing to the intersite Coulomb interaction, excitons appear in the optical spectra. These peaks are sensitive to the dimensionality of the electronic state. The dimerization, the anisotropy of transfer integrals and the intersite Coulomb interaction affect overall feature of collective excitation spectra.

I-T-6 Ab Initio Molecular Orbital, Hartree-Fock, and Exact Diagonalization Studies of Structures and Electronic Phases of (BEDT-TTF) Clusters and κ-(BEDT-TTF) Salts

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([1]*GUAS)*

[*J. Chem. Phys.* **111**, 5986 (1999)]

Electronic and geometrical structures of bis-(ethylenedithio)tetrathiafulvalene (BEDT-TTF) molecules are studied using ab initio molecular orbital methods. The optimized structure of a BEDT-TTF monomer is close to the experimental one within errors of 0.02 Å and 0.5 degree in bond length and angle, respectively, expect the ethylene group. Ab initio parameters such as transfer integrals and Coulomb interactions are determined from the BEDT-TTF dimer and tetramer calculations. Using model Hamiltonians with the ab initio parameters, we investigate the electronic states based on the exact diagonalization method. The results show that the ground state has antiferromagnetic correlation, which is consistent with experimental results. We study the effects of long-range Coulomb interactions employing the 2-D extended Hubbard model with the Hartree-Fock approximation. It is found that the ground state shows various phases; antiferromagnetic, charge ordering, and paramagnetic ones, controlled by the long-range interactions.

I-T-7 Two-Loop Renormalization-Group Analysis of Two-Dimensional Electron Systems

KISHINE, Jun-ichiro; FURUKAWA, Nobuo[1]**; YONEMITSU, Kenji**
([1]*Aoyama Gakuin Univ.)*

[*Recent Prog. Many-Body Theories* **3** submitted]

Recently there has been renewal of interest in understanding two-dimensional (2D) electron systems based on the renormalization-group (RG) framework. In these attempts, possible instabilities occurring in the system have been discussed based on the *one-loop* RG analysis and little attention has been given to the RG flow of the quasiparticle weight that is treated in the *two-loop* level. In this paper, we consider the two-dimensional electron systems where the two-loop RG analysis works well. We take up the following two examples. As the first example, we consider a 2D Fermi surface that consists of flat regions and round-arc regions. We found that the RG flow of the quasiparticle weight depends on the location of the electron wave number, **k**, on the Fermi surface due to the kinematical restriction to the logarithmically divergent processes in the flat regions of the Fermi surface. As the second example, we consider a 2D Fermi surface which touches the Umklapp surface at the 4 points (±π/2, ±π/2). In this case, growth of the umklapp processes between (±π/2, ±π/2) points cause the vanishing quasiparticle weight at these points.