RESEARCH ACTIVITIES I
Department of Theoretical Studies

I-A Theoretical Study and Design of Functional Molecular Systems: New Bonding, Structures, and Reactions

In theoretical and computational chemistry, it is an important goal to develop functional molecules with novel bonding and structures before or in cooperation with experiment. Thus, novel bonds and structures provided by heavier atoms are investigated, which are expected to serve as new building blocks for the design of functional molecules. In addition, unique spaces and flexible structures provided by large molecules and clusters are highly emphasized to develop functional molecular systems by modulating the electronic properties. Efficient computational methods are investigated to perform reliable quantum chemistry calculations of large molecular systems.

I-A-1 Counterion-Driven Spontaneous Polymerization of the Linear C_{60}^{n-} Chains in the fcc Fullerides and Its Magic Number Behavior

LU, Jing[1]; NAGASE, Shigeru; ZHANG, Shuang[2]; PENG, Lianmao[2]
([1]IMS and Peking Univ.; [1]Peking Univ.)

[*Chem. Phys. Lett.* **395**, 199–204 (2004)]

Polymerizatron of C_{60} has attracted considerable interest in recent years. By using the first principle energy band calculations, it is found that the injection of electron alone into C_{60} increases the instability of the polymeric C_{60} chain, despite a decrease in the polymerization energy barrier, and cannot cause a spontaneous polymerization as previously proposed. However, inclusion of the electrostatic attraction between the C_{60}^{n-} and counterions can dramatically stabilize the polymeric C_{60}^{n-} chains at $n = 1$ and 3, accompanied by a further decrease in the polymerization energy barrier, and eventually drives an observable spontaneous polymerization of the C_{60}^{n-} chains in the fcc fullerides at these two doping levels.

I-A-2 Amphoteric and Controllable Doping of Carbon Nanotubes by Encapsulation of Organic and Organometallic Molecules

LU, Jing[1]; NAGASE, Shigeru; YU, Dapeng[2]; YE, Hengqiang[2]; HAN, Rushan[2]; GAO, Zhengxiang[2]; ZHANG, Shuang[2]; PENG, Lianmao[2]
([1]IMS and Peking Univ.; [1]Peking Univ.)

[*Phys. Rev. Lett.* **93**, 116804 (4 pages) (2004)]

Single-wall carbon nanotubes (SWNTs) have attracted considerable interest as a possible application to molecular electronics. For this application, it is important to obtain both *p*- and *n*-type air-stable SWNTs and control their carrier densities. By performing density functional calculations, we show that controllable *p*- and *n*-type doping can be realized by tuning the electron affinities or ionization potentials of the organic and organometallic molecules encapsulated inside SWNTs. This novel type of SWNT-based material offers great promise for molecular electronics because of its air stability, synthetic simplicity and the abundance of organic and organometallic molecules.

I-A-3 Electronic Excited States and Stabilities of Fullerenes: Isomers of C_{78} and $Mg@C_{72}$

SLANINA, Zdenek; UHLÍK, Filip[1]; ADAMOWICZ, Ludwik[2]; KOBAYASHI, Kaoru; NAGASE, Shigeru
([1]Charles Univ.; [2]Univ. Arizona)

[*Int. J. Quantum Chem.* **100**, 610–616 (2004)]

There is one factor in relative stabilities of isomeric fullerenes that has rarely been studied so far—the contribution of excited electronic states. The contribution is clearly quantified by the electronic partition function, supposing the related excitation energies can be evaluated. As temperatures in fullerene synthesis are high, the term should be taken into account. In this article the problem is studied on two isomeric systems. One is the set of five isolated pentagon rule isomers of C_{78}, relatively well known from experiments. The other is a model set of four isomers of $Mg@C_{72}$ (not isolated yet). It is found that the electronic partition function can cause significant changes in the computed equilibrium relative concentrations of isomers at high temperatures.

I-A-4 1,6,7-Trigermabicyclo[4.1.0]hept-3-en-7-yl: The Isolable Bicyclic Germyl Radical

ISHIDA, Yutaka[1]; SEKIGUCHI, Akira[1]; KOBAYASHI, Kaoru; NAGASE, Shigeru
([1]Univ. Tsukuba)

[*Organometallics* **23**, 4891–4896 (2004)]

The one-electron oxidation reaction of potassium 3,4-dimethyl-1,6,7-tris(tri-tert-butylsilyl)-1,6,7-trigermabicyclo[4.1.0]hept-3-en-7-ide with tris(pentafluorophenyl)borane in THF results in the formation of stable 3,4-dimethyl-1,6,7-tris(tri-tert-butylsilyl)-1,6,7-trigermabicyclo-[4.1.0]hept-3-en-7-yl, representing the first bicyclic germyl radical with the bicyclo[4.1.0]-

hept-3-ene skeleton. The electronic and structural aspects of the germyl radical were characterized by density functional calculations as well as X-ray crystallographic analysis and ESR spectroscopy.

I-A-5 Isolation of a *Se*-Nitrososelenol: A New Class of Reactive Nitrogen Species Relevant to Protein *Se*-Nitrosation

SHIMADA, Keiichi[1]; GOTO, Kei[1]; KAWASHIMA, Takayuki[1]; TAKAGI, Nozomi; CHOE, Yoong-Kee; NAGASE, Shigeru
([1]Univ. Tokyo.)

[*J. Am. Chem. Soc.* **126**, 13238–13239 (2004)]

Nitric oxide (NO) is a messenger molecule implicated in a number of physiological processes. In several recent reports, it has been suggested that the interactions of NO (or NO-derived species) with the SeH groups of selenoproteins are involved in NO-mediated cellular functions. To elucidate the mechanism of NO-meditated modification of selenoproteins, a stable Se-nitrosated derivative of an organoselenol, a Se-nitososelenol (RseNO) is successfully synthesized. The observed ^{77}Se NMR and UV-vis spectra are analyzed by the gauge-including atomic orbital (GIAO) calculations at the B3LYP/6-311G (3d)[Se]:6-311G(d)[C, O, N, H]/B3LYP/6-31G(d) level and time-dependent density functional (TD-DFT) calculations at the B3LYP/6-311+G(2d)/B3LYP/6-31G(d) levels, respectively.

I-A-6 A New Approach to Simulate the Depolymerization Process of a Two-Dimensional Hexagonal C_{60} Polymer

LU, Jing[1]; NAGASE, Shigeru; ZHANG, Shuang[2]; PENG, Lianmao[2]
([1]IMS and Peking Univ.; [2]Peking Univ.)

[*Chem. Phys. Lett.* **398**, 486–488 (2004)]

In a recent study, the depolymerization process of a two-dimensional hexagonal C_{60} polymer was modeled by increasing stepwise the lattice constant, and a considerably high barrier for polymerization was calculated. In the present study, all degrees of freedom (including the lattice constant) are allowed to relax for each distance between fullerenes in order to simulate the depolymerization process of a two-dimensional hexagonal C_{60} polymer. The resulting depolymerization barrier is significantly improved compared with the previous study in which the lattice constant was fixed though the atomic positions were relaxed.

I-A-7 Chemical Reactivity and Redox Property of $Sc_3@C_{82}$

WAKAHARA, Takatsugu[1]; SAKURABA, Akihiro[2]; IIDUKA, Yuko[1]; OKAMURA, Mutsuo[2]; TSUCHIYA, Takahiro[1]; MAEDA, Yutaka[1]; AKASAKA, Takeshi[1]; OKUBO, Shingo; KATO, Tatsuhisa; KOBAYASHI, Kaoru; NAGASE, Shigeru; KADISH, Karl M.[3]
([1]Univ. Tsukuba; [2]Niigata Univ.; [3]Univ. Houston)

[*Chem. Phys. Lett.* **398**, 553–556 (2004)]

The redox property of $Sc_3@C_{82}$ is investigated by using disilirane as a chemical probe. The redox potential of $Sc_3@C_{82}$ in *o*-dichlorobenzene shows a high reactivity attributable to its high electron-accepting and -donating ability. No ESR signal is observed at room temperature for $Sc_3@C_{82}$ in the presence of pyridine, indicating formation of the diamagnetic $Sc_3@C_{82}$ anion. The diamagnetic $Sc_3@C_{82}$ anion is also prepared electrochemically in 1,2-dichlorobenzene. The reactivity and redox properties of $Sc_3@C_{82}$ are characterized by calculating the electron affinity and ionization potentials using density functional theory.

I-A-8 Reduction of Endohedral Metallofullerenes: A Convenient Method for Isolation

TSUCHIYA, Takahiro[1]; WAKAHARA, Takatsugu[1]; SHIRAKURA, Shingo[2]; MAEDA, Yutaka[1]; AKASAKA, Takeshi[1]; KOBAYASHI, Kaoru; NAGASE, Shigeru; KATO, Tatsuhisa; KADISH, Karl M.[3]
([1]Univ. Tsukuba; [2]Niigata Univ.; [3]Univ. Houston)

[*Chem. Mater.* **16**, 4343–4346 (2004)]

Isolation of endohedral metallofullerenes has been often carried out using a multistage high-performance liquid chromatography (HPLC) method. However, this method is tedious and time-consuming work, making it difficult to obtain macroscopic quantities of pure endohedral metallofullerene samples. We report herein a selective electrochemical reduction of endohedral metallofullerenes from extracts of carbon soot and a convenient separation method of endohedral metallofullerenes and empty fullerenes. A chemical oxidation of the endohedral metallofullerene anions is also discussed.

I-A-9 Dispersion of Single-Walled Carbon Nanotube Bundles in Nonaqueous Solution

MAEDA, Yutaka[1]; KIMURA, Shin-ichi[2]; HIRASHIMA, Yuya[1]; KANDA, Makoto[1]; LIAN, Yongfu[2]; WAKAHARA, Takatsugu[2]; AKASAKA, Takeshi[2]; HASEGAWA, Tadashi[1]; TOKUMOTO, Hiroshi[3]; SHIMIZU, Tetsuo[4]; KATAURA, Hiromichi[4]; MIYAUCHI, Yuhei[5]; MARUYAMA, Shigeo[5]; KOBAYASHI, Kaoru; NAGASE, Shigeru
([1]Tokyo Gakugei Univ.; [2]Univ. Tsukuba; [3]Hokkaido Univ.; [4]AIST; [5]Univ. Tokyo)

[*J. Phys. Chem. B* **108**, 18395–18397 (2004)]

Although single-walled carbon nanotubes (SWNTs) have interesting mechanical and electrical properties, their practical applications have been hindered by the poor dispersibility and solubility. Therefore, the effective dispersion of bundled SWNTs in organic solvents is important, which makes homogenious chemical reactions possible. We report the observation of photoluminescence from SWNTs dispersed in a tetrahydrofuran(THF)/octylamine solution, providing the first clear evidence for individual SWNTs in nonaqueous solution. We also report the effective amine-assisted dispersion of C_{60} and La@C_{82} peapods. This solution phase handling is applicable to the analysis of the electronic properties and modification of SWNTs and peapods.

I-A-10 Regioselective Carbon–Carbon Bond Cleavage of an Open-Cage Diketone Derivative of [60]Fullerene by Reaction with Aromatic Hydrazones

IWAMATSU, Sho-ichi[1]; KUWAYAMA, Toshiki[1]; KOBAYASHI, Kaoru; NAGASE, Shigeru; MURATA, Shizuaki[1]
([1]Nagoya Univ.)

[*Synthesis* 2962–2964 (2004)]

Opening a hole on the fullerene cage by a controlled carbon–carbon bond cleavage is of current interest. It is found that the addition of an aromatic hydrazone to the diketone derivative of C_{60} takes place with a regioselective C–C bond scission, which leads to a ring-expanded product having a 16-membered ring orifice.

I-A-11 Gibbs Energy-Based Treatment of Metallofullerenes: Ca@C_{72}, Ca@C_{74}, Ca@C_{82}, and La@C_{82}

SLANINA, Zdenek[1]; ADAMOWICZ, Ludwik[2]; KOBAYASHI, Kaoru; NAGASE, Shigeru
([1]IMS and Academia Sinica; [2]Univ. Arizona)

[*Mol. Sim.* **31**, 71–77 (2005)]

The paper surveys ongoing computations on endohedral fullerene systems, combining the treatments of quantum chemistry and statistical mechanics. Relative concentrations of four isomers of Ca@C_{72}, six isomers of Ca@C_{74}, nine isomers of Ca@C_{82}, and four isomers of La@C_{82} are evaluated using the Gibbs energy based on density-functional theory computations. The results illustrate the enthalpy–entropy interplay in the systems produced under high temperatures. Approximations for description of the encapsulate motions are analyzed.

I-A-12 Chemical Reactivities of the Cation and Anion of M@C_{82} (M = Y, La, and Ce)

MAEDA, Yutaka[1]; MIYASHITA, Jun[1]; HASEGAWA, Tadashi[1]; WAKAHARA, Takatsugu[2]; TSUCHIYA, Takahiro[2]; FENG, Lai[2]; LIAN, Yongfu[2]; AKASAKA, Takeshi[2]; KOBAYASHI, Kaoru; NAGASE, Shigeru; KAKO, Masahiro[3]; YAMAMOTO, Kazunori[4]; KADISH, Karl M.[5]
([1]Tokyo Gakugei Univ.; [2]Univ. Tsukuba; [3]Univ. Electro-Communications; [4]Japan Nuclear Fuel Cycle Development Inst.; [5]Univ. Houston)

[*J. Am. Chem. Soc.* **127**, 2143–2146 (2005)]

The chemical reduction and oxidation of M@C_{82} (M = Y, La, and Ce) afford the corresponding anion and cation, respectively, which show unique and interesting chemical reactivities. It is found that the successful reversible gain or loss of electrons by ionization is useful for controlling the stability and reactivity of M@C_{82} toward both nucleophiles and electrophiles. The reactivity is discussed by calculating the HOMO and LUMO energy levels.

I-A-13 Systematic Studies on Redox Behavior of Homonuclear Double-Bond Compounds of Heavier Group 15 Elements

SASAMORI, Takahiro[1]; MIEDA, Eiko[1]: NAGAHORA, Noriyoshi[1]; TAKEDA, Nobuhiro[1]; TAKAGI, Nozomi; NAGASE, Shigeru; TOKITOH, Norihiro[1]
([1]Kyoto Univ.)

[*Chem. Lett.* 166–167 (2005)]

Stable double bonds between heavier group 15 elements have long attracted considerable interest in main group chemistry. The electronic properties of RE=ER (E = P, Sb, and Bi; R = 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)6-methyl]phenyl) synthesized recently are systematically investigated based on the measurement of cyclic voltammetry and density functional calculations. It is emphasized that relativistic effects are very important for the systematic understanding of the nature of double bonds in RM=MR.

I-A-14 Syntheses and Structures of Hypervalent Pentacoordinate Carbon and Boron Compounds Bearing an Anthracene Skeleton—Elucidation of Hypervalent Interaction Based on X-Ray Analysis and DFT Calculation

YAMASHITA, Makoto[1]; YAMAMOTO, Yohsuke[1]; AKIBA, Kin-ya[2]; HASHIZUME, Daisuke[3]; IWASAKI, Fujiko[3]; TAKAGI, Nozomi; NAGASE, Shigeru
([1]Hiroshima Univ.; [2]Waseda Univ.; [3]Univ. Electro-Communications)

[*J. Am. Chem. Soc.* **127**, 4354–4371 (2005)]

Pentacoordinate and tetracoordinate carbon and boron compounds bearing an anthracene skeleton with two oxygen or nitrogen atoms at the 1,8-positions are synthesized by the use of four newly synthesized tridentate ligand precursors, and characterized by X-ray crystallographic analysis. To provide theoretical insight into the nature of hypervalent interactions, the topology of electron density distributions around hypervalent bonds is analyzed using density functional calculations and X-ray results. The existence of weak apical hypervalent bonds of considerable ionic character is reported.

I-A-15 Adsorption Configuration of NH_3 on Single-Wall Carbon Nanotubes

LU, Jing[1]; NAGASE, Shigeru; MAEDA, Yutaka[2]; WAKAHARA, Takatsugu[3]; NAKAHODO, Tsukasa[3]; AKASAKA, Takeshi[3]; YU, Dapeng[4]; GAO, Zhengxiang[4]; HAN, Rushan[4]: YE, Hengqiang[4]
([1]IMS and Peking Univ.; [2]Tokyo Gakugei Univ.; [3]Univ. Tsukuba; [4]Peking Univ.)

[*Chem. Phys. Lett.* **405**, 90–92 (2005)]

The electronic properties of single-wall carbon nanotubes (SWNTs) are significantly changed when NH_3 molecules are adsorbed on the surface of SWNTs. Density functional calculations show that the absorption energies depend on the electronic structures of SWNTs that are metallic or semiconducting. Metallic SWNTs interact more strongly with NH_3 than semiconducting SWNTs, when comparison is made for SWNTs having similar diameters. Hydrogen-bond-like links dominate the attraction between NH_3 and SWNTs.

I-A-16 Structural Characterization of $Y@C_{82}$

FENG, Lai[1]; WAKAHARA, Takatsugu[1]; TSUCHIYA, Takahiro[1]; MAEDA, Yutaka[2]; LIAN, Yongfu[1]; AKASAKA, Takeshi[1]; MIZOROGI, Naomi; KOBAYASHI, Kaoru; NAGASE, Shigeru; KADISH, Karl M.[3]
([1]Univ. Tsukuba; [2]Tokyo Gakugei Univ.; [3]Univ. Houston)

[*Chem. Phys. Lett.* **405**, 274–277 (2005)]

The cation and anion of $Y@C_{82}$ are prepared by controlled potential electrolysis, and their stabilities are investigated. The anion is found to be much more stable than the cation under an air atmosphere. These are confirmed by performing theoretical calculations. It is determined that the cage structure of $Y@C_{82}$ has C_{2v} symmetry by observing the ^{13}C NMR spectrum of the stable diamagnetic anion. This agrees well with theoretical prediction.

I-A-17 Synthesis and Characterization of Exohedrally Silylated $M@C_{82}$ (M = Y and La)

YAMADA, Michio[1]; FENG, Lai[1]; WAKAHARA, Takatsugu[1]; TSUCHIYA, Takahiro[1]; MAEDA, Yutaka[2]; LIAN, Yongfu[1]; KAKO, Masahiro[3]; AKASAKA, Takeshi[2]; KATO, Tatsuhisa[4]; KOBAYASHI, Kaoru; NAGASE, Shigeru
([1]Univ. Tsukuba; [2]Tokyo Gakugei Univ.; [3]Univ. Electro-Communications; [4]Josai Univ.)

[*J. Phys. Chem. B* **109**, 6049–6051 (2005)]

The silylation of endohedral mono-metallofullerenes ($Y@C_{82}$ and $La@C_{82}$) is carried out, and the adducts are isolated by HPLC separation. As the first examples of the tuning of electronic properties of mono-metallofullerenes by exohedral addition, it is shown that the bis-silylated derivatives of $Y@C_{82}$ and $La@C_{82}$ have significantly lower oxidation and higher reduction potentials than $Y@C_{82}$ and $La@C_{82}$. Bis-silylation is very effective for modifying the electronic properties of endohedral metallofullerenes as well as empty fullerenes.

I-A-18 Synthesis and Characterization of Stable Hypervalent Carbon Compounds (10-C-5) Bearing a 2,6-Bis(*p*-substituted phenyloxymethyl)benzene Ligand

AKIBA, Kin-ya[1]; MORIYAMA, Yuji[2]; MIZOZOE, Mitsuhiro[2]; INOHARA, Hideki[2]; NISHII, Takako[2]; YAMAMOTO, Yohsuke[2]; MINOURA, Mao[2]; HASHIZUME, Daisuke[3]; IWASAKI, Fujiko[3]; TAKAGI, Nozomi; ISHIMURA, Kazuya; NAGASE, Shigeru
([1]Waseda Univ.; [2]Hiroshima Univ.; [3]Univ. Electro-Communications)

[*J. Am. Chem. Soc.* **127**, 5893–5901 (2005)]

Stable hypervalent carbon compounds (10-C-5) bearing a 2,6-bis(*p*-tolyloxymethyl)benzene ligand are synthesized and their structures are characterized by X-ray analysis and theoretical calculations. Among these, sterically flexible compounds bearing two O (*p*-Tol) groups or two O (p-$CH_3OC_6H_4$) groups take symmetrical structures with two almost equal C–O distances. The electron density distribution analysis by accurate X-ray measurements and theoretical calculations show that the central carbon atom forms a weak and ionic hypervalent bond with the two oxygen atoms, as suggested by the small electron density ($\rho(r)$) and small positive Laplacian ($\nabla^2\rho(r)$) values at the bond critical points.

I-A-19 Practical Performance Assessment of Accompanying Coordinate Expansion Recurrence Relation Algorithm for Computation of Electron Repulsion Integrals

KATOUDA, Michio; KOBAYASHI, Masato[1]; NAKAI, Hiromi[1]; NAGASE, Shigeru
([1]Waseda Univ.)

[*J. Theor. Cpmput. Chem.* **4**, 139–149 (2005)]

In the applications of molecular orbital and density functional methods, it is considerably time-consuming to calculate two-electron repulsion integrals for large molecular systems. A program code is developed to calculate effectively electron repulsion integrals based on the accompanying coordinate expansion recurrence relation (ACE-RR) algorithm. The present ACE-RR method is comparable to or at most 30% faster than the Pople–Hehre method. Furthermore, the ACE-RR method is drastically faster than the Dupuis–Rys–King method when the contraction of basis sets is high.

I-A-20 2D NMR Characterization of the $La@C_{82}$ Anion

TSUCHIYA, Takahiro[1]; WAKAHARA, Takatsugu[1];

MAEDA, Yutaka[2]; AKASAKA, Takeshi[1]; WAELCHLI, Markus[3]; KATO, Tatsuhisa[4]; OKUBO, Hiroshi[5]; MIZOROGI, Naomi; KOBAYASHI, Kaoru; NAGASE, Shigeru
([1]Univ. Tsukuba; [2]Tokyo Gakugei Univ.; [3]Bruker Boispin, Co. Ltd.; [4]Josai Univ.; [5]Toyo Tanso Co. Ltd.)

[*Angew. Chem., Int. Ed.* **44**, 3282–3285 (2005)]

NMR spectroscopy has been very often employed as a powerful tool for elucidating the cage symmetry of endohedral metallofullerenes. However, it remains an important goal to verify the bond connectivity and assign the NMR lines, as this is essential for full structural characterization of endohedral metallofullerenes. As the fist example for metallofullerenes, the mapping of the bond connectivity in the carbon cage of the La@C_{82} anion and definitive assignment of the NMR lines are reported with the help of density functional calculations. It is suggested that the 2D INADEQUATE (incredible natural abundance double quantum transfer experiment) NMR measurement can be used as an alternative method to X crystallographic analysis for the structural characterization of endohedral metallofullerenes.

I-A-21 Open-Cage Fullerene Derivatives Suitable for the Encapsulation of a Hydrogen Molecule

IWAMATSU, Sho-ichi[1]; MURATA, Shizuaki[1]; ANDOH, Yukihiro[1]; MINOURA, Masayuki[1]; KOBAYASHI, Kaoru; MIZOROGI, Naomi; NAGASE, Shigeru
([1]Nagoya Univ.)

[*J. Org. Chem.* **70**, 4820–4825 (2005)]

The encapsulation of a hydrogen molecule into an open-cage fullerene having a 16-membered ring orifice is successfully performed. The efficiency of encapsulation depends strongly on both H_2 pressure and temperature. The encapsulated H_2 molecule is released by heating. The activation energy barriers for this process are determined to be 22–24 kcal/mol. From the differential scanning calorimetry measurement and density functional calculations, it is discussed whether the encapsulated H_2 molecule is stabilized or destabilized inside the open-cage fullerene.

I-A-22 Computed Structure and Energetics of La@C_{60}

SLANINA, Zdenek; LEE, Shyi-Long[1]; ADAMOWICZ, Ludwik[2]; UHLÍK, Filip[3]; NAGASE, Shigeru
([1]Natl. Chung-Cheng Univ.; [2]Univ. Arizona; [3]Charles Univ.)

[*Int. J. Quantum. Chem.* **104**, 272–277 (2005)]

The molecular and electronic structures of La@C_{60} are investigated by density functional calculations. The La atom is not located in the cage center, but is shifted toward the wall. There is a substantial charge transfer from La to C_{60}, at some levels of theory amounting roughly to three electrons. A larger binding energy is calculated for La@C_{60}. However, the entropy term also influences the association equilibrium significantly, so that the standard Gibbs-energy change depends strongly on temperature. The reasons why La@C_{60} could not be isolated yet are briefly discussed, as well as a possible relationship to superconductivity.

I-A-23 Metallic Phase in the Metal-Intercalated Higher Fullerene $Rb_{8.8(7)}C_{84}$

RIKIISHI, Yoshie[1]; KASHINO, Yoko[1]; KUSAI, Haruka[1]; TAKABAYASHI, Yasuhiro[1]; KUWAHARA, Eiji[1]; KUBOZONO, Yoshihiro[1,2]; KAMBE, Takashi[1]; TAKENOBU, Taishi[3]; IWASA, Yoshihiro[3]; MIZOROGI, Naomi; NAGASE, Shigeru; OKADA, Susumu[2]
([1]Okayama Univ.; [2]Univ. Tsukuba; [3]Tohoku Univ.)

[*Phys. Rev. B* **71**, 224118 (6 pages) (2005)]

A new material of higher fullerene, Rb_xC_{84}, is synthesized by intercalating Rb metals into C_{84} crystals. The Rb_xC_{84} crystals show a simple cubic (sc) structure with lattice constants of 16.82(2) Å at 6.5 K and 16.87(2) Å at 295 K. The Rietveld refinements are achieved with the space group, $Pa3$, based on a model that the C_2 axis of D_{2d}-C_{84} aligned along [111]. The sample composition is determined to be $Rb_{8.8(7)}C_{84}$. The ESR spectrum at 303 K is composed of a broad peak with a peak-to-peak linewidth of ΔH_{pp} = 220 G and a narrow peak with ΔH_{pp} = 24 G. Temperature dependence of the broad peak clearly show a metallic behavior. The metallic behavior is discussed based on theoretical calculations.

I-A-24 Interplay of Single-Wall Carbon Nanotubes and Encapsulated La@C_{82}, La_2@C_{80}, and Sc_3N@C_{80}

LU, Jing[1]; NAGASE, Shigeru; RE, Suyong; ZHANG, Xinwei[2]; YU, Dapeng[3]; ZHANG, Jin[3]; HAN, Rushan[3]; GAO, Zhengxiang[3]; YE, Hengqiang[3]; ZHANG, Shuang[3]; PENG, Lianmao[3]
([1]IMS and Peking Univ.; [2]Inst. Appl. Phys. Comput. Math.; [3]Peking Univ.)

[*Phys. Rev. B* **71**, 235417 (5 pages) (2005)]

Encapsulation of endohedral metallofullerenes (La@C_{82}, La@C_{80}, and Sc_3N@C_{80}) inside single-wall carbon nanotubes (SWNTs) is investigated by using first-principles calculations. It is found that La@C_{82}, La_2@C_{80}, and Sc_3N@C_{80} are endothermically encapsulated inside (17,0) SWNT, while they are exothermically encapsulated inside the (14,7) and (19,0) SWNTs. Electron transfer takes place from SWNTs to strongly electrophilic La@C_{82} and La_2@C_{80}. Dependent on the tube chirality, the Van Hove singularity positions of SWNT is significantly shifted by a local 3% radial strain induced by the insertion of metallofullerenes.

I-A-25 Structural Evolution of [2+1] Cycloaddition Derivatives of Single-Wall Carbon Nanotubes: From Open Structure to Closed Three-Membered Ring Structure with Increasing Tube Diameter

LU, Jing[1]; NAGASE, Shigeru; ZHANG, Xinwei[2]; MAEDA, Yutaka[3]; WAKAHARA, Takatsugu[4]; NAKAHODO, Tsukasa[4]; TSUCHIYA, Takahiro[4]; AKASAKA, Takeshi[4]; YU, Dapeng[5]; GAO, Zhengxiang[5]; HAN, Rushan[5]; YE, Hengqiang[5]
([1]IMS and Peking Univ.; [2]Inst. Appl. Phys. Computational Math.; [3]Tokyo Gakugei Univ.; [4]Univ. Tsukuba; [5]Peking Univ.)

[*THEOCHEM* **725**, 255–257 (2005)]

Sidewall functionalization of single-wall carbon nanotubes (SWNTs) is currently of considerable interest. By using density functional theory calculations, it is found that the [2+1] cycloaddition derivatives of the armchair (m,m) SWNTs evolve from an open structure to a closed three-membered ring structure when $m > 11$ for NH addition, $m > 10$ for O and CH_2 additions, and $m > 5$ for SiH_2 addition. The diameter upper limit of the opening of the sidewall of SWNTs upon [2+1] cycloaddition is predicted to be about 15 Å.

I-A-26 Missing Metallofullerene La@C_{74}

NIKAWA, Hidefumi[1]; KIKUCHI, Takashi[1]; WAKAHARA, Takatsugu[1]; HAKAHODO, Tsukasa[1]; TSUCHIYA, Takahiro[1]; RAHMAN, G. M. Aminur[1]; AKASAKA, Takeshi[1]; MAEDA, Yutaka[2]; YOZA, Kenji[3]; HORN, Ernst[4]; YAMAMOTO, Kazunori[5]; MIZOROGI, Naomi; NAGASE, Shigeru
([1]Univ. Tsukuba; [2]Tokyo Gakugei Univ.; [3]Bruker AXS K. K.; [4]Rikkyo Univ.; [5]Power Reactor Nuclear Fuel Development Co.)

[*J. Am. Chem. Soc.* **127**, 9684–9685 (2005)]

Since the first extraction of La@C_{82} in 1991, many soluble endohedral metallofullerenes have been separated and characterized. However, insoluble metallofullerenes such as La@C_{60} and La@C_{74} have not yet been isolated. The missing La@C_{74} is isolated as a stable derivative, La@C_{74} ($C_6H_3Cl_2$). The structure is determined by X-ray crystallographic analysis and the properties are discussed on the basis of theoretical calculations. La@C_{74} has considerable radical character on the C_{74} (D_{3h}) surface, and is trapped by the dichlorophenyl radical produced during extraction.

I-A-27 Chemical Reactivity of Sc_3N@C_{80} and La_2@C_{80}

IIDUKA, Yuko[1]; IKENAGA, Ozora[1]; SAKURABA, Akihiro[2]; WAKAHARA, Takatsugu[1]; TSUCHIYA, Takahiro[1]; MAEDA, Yutaka[3]; NAKAHODO, Tsukasa[1]; AKASAKA, Takeshi[1]; KAKO, Masahiro[4]; MIZOROGI, Naomi; NAGASE, Shigeru
([1]Univ. Tsukuba; [2]Niigata Univ.; [3]Tokyo Gakugei Univ.; [4]Univ. Electro-Communications)

[*J. Am. Chem. Soc.* **127**, 9956–9957 (2005)]

For both Sc_3N@C_{80} and La_2@C_{80}, the carbon cage originates from the I_h isomer of C_{80} and has an electronic structure described as $C_{80}{}^{6-}$. Despite this similarity, it is found that Sc_3N@C_{80} has a much lower thermal reactivity toward disilirane than La_2@C_{80}. This is the first example of reactivity difference caused by endohedral species. Theoretical calculations show that Sc_3N@C_{80} and La_2@C_{80} have almost the same HOMO levels. However, Sc_3N@C_{80} has a much higher LUMO level than La_2@C_{80}. The LUMO of Sc_3N@C_{80} is delocalized not only on the Sc_3N cation but also on the $C_{80}{}^{6-}$ cage. In contrast, the LUMO of La_2@C_{80} is localized on the two La^{3+} cation and is more suitable as an electron accommodation.

I-A-28 Large-Scale Separation of Metallic and Semiconducting Single-Walled Carbon Nanotubes

MAEDA, Yutaka[1]; KIMURA, Shin-ichi[2]; KANDA, Makoto[1]; HIRASHIMA, Yuya[1]; HASEGAWA, Tadashi[1]; WAKAHARA, Takatsugu[2]; LIAN, Yongfu[2]; NAKAHODO, Tsukasa[2]; TSUCHIYA, Takahiro[2]; AKASAKA, Takeshi[2]; LU, Jing[3]; ZHANG, Xinwei[3]; GAO, Zhengxiang[3]; YU, Yapeng[3]; NAGASE, Shigeru; KAZAOUI, Said[4]; MINAMI, Nobutsugu[4]; SHIMIZU, Tetsuo[4]; TOKUMOTO, Hiroshi[5]; SAITO, Riichiro[6]
([1]Tokyo Gakugei Univ.; [2]Univ. Tsukuba; [3]Peking Univ.; [4]AIST; [5]Hokkaido Univ.; [6]Tohoku Univ.)

[*J. Am. Chem. Soc.* **127**, 10287–10290 (2005)]

In the applications of single-walled carbon nanotubes (SWNTs), it is extremely important to separate semiconducting and metallic SWNTs. Although several methods have been reported for the separation, only low yields have been achieved at great expense. Theoretical calculations confirm that metallic SWNTs are more strongly adsorbed by amines than semiconducting SWNTs and the adsorbed amines are removable after separation because of the small absorption energies. Based on this confirmation, we have developed a separation method involving a dispersion-centrifugation process in a tetrahydrofuran solution of amine, which makes metallic SWNTs highly concentrated to 87% in a simple way.

I-A-29 Encapsulation of La@C_{82} and La_2@C_{80} inside Single-Walled Boron Nitride Nanotubes

SONG, Wei[1]; NI, Ming[1]; LU, Jing[1]; GAO, Zhengxiang[1]; NAGASE, Shigeru; YU, Dapeng[1]; YE, Hengqiang[1]; ZHANG, Xinwei[2]
([1]Peking Univ.; [2]Inst. Appl. Phys. Computational Math.)

[*THEOCHEM* **730**, 119–122 (2005)]

As a new type of boron and nitrogen peapods, the possible encapsulation of endohedral metallofullerenes inside single-walled boron nitride nanotubes (BNNTs) is investigated by first-principle calculations, to make comparison with the corresponding carbon peapods. It is found that La@C_{82} and La_2@C_{80} can be exothermically encapsulated inside the (17,0) and (14,7) BNNTs. The minimum diameter for exothermic encapsulation is predicted to be 13.5 Å. The features of band structures are also discussed.

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

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

I-B-1 Classification and Prediction of Low-Energy Membrane Protein Helix Configurations by Replica-Exchange Monte Carlo Method

KOKUBO, Hironori[1]**; OKAMOTO, Yuko**
([1]SOKENDAI)

[*J. Phys. Soc. Jpn.* **73**, 2571 (2004)]

The effectiveness of our classification and prediction method for transmembrane helix configurations of membrane proteins by replica-exchange simulations is tested with glycophorin A transmembrane dimer. Replica-exchange simulations can sample wide configurational space without getting trapped in local-minimum free energy states and we can find stable structures at low temperatures. We classify low-energy configurations into clusters of similar structures by the principal component analysis. These clusters are identified as the global- and local-minimum free energy states. Our classifications revealed that there are only two major groups of similar structures in the case of the simulation with the dielectric constant $\varepsilon = 1.0$ and five such groups in the case of $\varepsilon = 4.0$. The global-minimum free energy state in the case of $\varepsilon = 1.0$ is very close to the structure of the NMR experiments and the prediction was successful, while in the case of $\varepsilon = 4.0$ not the global-minimum but a local-minimum free energy state corresponds to the native structure. It is shown that the global-minimum free energy state at low temperatures is also the global-minimum potential energy state in both cases.

I-B-2 Combination of the Replica-Exchange Monte Carlo Method and the Reference Interaction Site Model Theory for Simulating a Peptide Molecule in Aqueous Solution

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

[*J. Phys. Chem. B* **108**, 19002 (2004)]

This article reports the first attempt to combine the replica-exchange Monte Carlo method and the reference interaction site model (RISM) theory for simulating a peptide molecule in aqueous solution. The energy function is the sum of the conformational energy and the solvation free energy. The solvation free energy for a fixed conformation of the peptide molecule is calculated using the RISM theory. The replica-exchange method is modified so that the dependence of the energy function on the temperature can be incorporated. The effectiveness of the combined approach is demonstrated for Met-enkephalin in water. It is argued that the number of replicas required for a peptide molecule immersed in water is drastically reduced by employing the combined approach. Solvation properties of Met-enkephalin are discussed and the free energy surface in gas phase is compared with that in water.

I-B-3 Multi-Overlap Molecular Dynamics Methods for Biomolecular Systems

ITOH, Satoru G.[1]**; OKAMOTO, Yuko**
([1]SOKENDAI)

[*Chem. Phys. Lett.* **400**, 308 (2004)]

We propose a molecular dynamics method for the multi-overlap algorithm. By utilizing a non-Boltzmann weight factor, this method realizes a random walk in the overlap space at a constant temperature and explores widely in the configurational space, where the overlap of a configuration with respect to a reference state is a measure for structural similarity. We can obtain detailed information about the free-energy landscape and the transition states among any specific reference conformations at that temperature. We also introduce a multi-dimensional extension of the multi-overlap algorithm. Appling this multi-dimensional method to a penta peptide, Met-enkephalin, we demonstrate its effectiveness.

I-B-4 Secondary-Structure Preferences of Force Fields for Proteins Evaluated by Generalized-Ensemble Simulations

YODA, Takao[1]**; SUGITA, Yuji**[2]**; OKAMOTO, Yuko**
([1]Nagahama Inst. Bio-Sci. Tech.; [2]Univ. Tokyo)

[*Chem. Phys.* **307**, 269 (2004)]

Secondary-structure forming tendencies are examined for six well-known protein force fields: AMBER-94, AMBER96, AMBER99, CHARMM22, OPLS-AA/L, and GROMOS96. We performed generalized-ensemble molecular dynamics simulations of two peptides. One of these peptides is C-peptide of ribonuclease A, and the other is the C-terminal fragment from the B1 domain of streptococcal protein G. The former is known to form α-helix structure and the latter β-hairpin structure by experiments. The simulation results revealed significant differences of the secondary-structure forming tendencies among the force fields. Of the six force fields, the results of AMBER99 and CHARMM22 were in accord with experiments for C-peptide. For G-peptide, on the other hand, the results of OPLS-AA/L and GROMOS96 were most consistent with experiments. Therefore, further improvements on the force fields are necessary for studying the protein folding problem from the first principles, in which a single force field can be used for all cases.

I-C Development of Simulation Algorithms for Complex Systems

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

I-C-1 Liquid-Gas Phase Transitions Studied by Multibaric-Multithermal Monte Carlo Simulations

OKUMURA, Hisashi; OKAMOTO, Yuko

[*J. Phys. Soc. Jpn.* **73**, 3304 (2004)]

We investigate the liquid-gas phase transition of a Lennard-Jones 12-6 potential system by the multibaric-multithermal Monte Carlo algorithm. The advantage of this method is that one can sample configurational space both in the gas phase and in the liquid phase from only one simulation run. Our liquid-gas coexistence data agree well with those obtained previously by other methods. We also show that this method is efficient in investigation of the transition state, which is the saddle point of a free energy surface.

I-D Other Results on Molecular Simulations

I-D-1 Comparisons between a Molecular Dynamics and Hydrodynamics Treatment of Non-Stationary Thermal Processes in a Liquid

OKUMURA, Hisashi; HEYES, David M.[1]
([1]Univ. Surrey)

[*Phys. Rev. E* **70**, 061206 (2004)]

Molecular dynamics (MD) and Navier-Stokes hydrodynamics have been performed to model thermal relaxation processes arising from an initially established nonequilibrium stationary state. A nanoscale two-layer Lennard-Jones (LJ) liquid system was constructed in which the two parts were initially at a different temperature, with a narrow transitional zone between the two layers which was spatially linear in temperature. The highest temperature layer had widths of 5 or 20 LJ particle diameters. The hydrodynamics model used parameterized MD-derived transport coefficients and the LJ equation of state as input functions. The temporal and spatial temperature and density profiles produced by the two methods show good agreement, indicating that a hydrodynamics description is reliable even for non-stationary phenomena down to the scale of a few molecular diameters.

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

I-E-1 Nonadiabatic Transition and Chemical Dynamics: Multi-Dimensional Tunneling Theory and Applications of the Zhu-Nakamura Theory

NAKAMURA, Hiroki

[*J. Theor. Comput. Chem.* **4**, 127 (2005)]

Tunneling and nonadiabatic transition are the most important quantum mechanical effects in chemical dynamics. They are important not only for understanding the dynamics properly, but also for controlling molecular functions. The Zhu-Nakamura (ZN) theory can be combined with the quasi-classical trajectory method and with the IVR (Initial Value Representation)-type semiclassical theory to deal with large chemical systems. Laser control of molecular processes and control of molecular functions can also be realized by properly controlling nonadibatic transitions. Furthermore, we have recently formulated an accurate theory for evaluating tunneling splitting and tunneling decay rate in multi-dimensional systems and also developed an efficient method to find caustics in multi-dimensional space. These methods combined with the ZN theory are expected to clarify various large scale chemical dynamics. This is a short review article on our recent activities mentioned above.

I-E-2 Electron Transfer Rate to Cover the Whole Range from Adiabatic to Nonadiabatic Regime Based on the Zhu-Nakamura Theory

ZHAO, Yi[1]; NAKAMURA, Hiroki
([1]IMS and Univ. Sci. Tech. China, China)

A new formula for electron transfer is formulated to bridge the gap between the adiabatic and nonadiabatic limits. The key point is to reformulate the prefactor of the famous Marcus formula by using the Zhu-Nakamura theory of nonadiabatic transition. It is shown that the new formula gives an excellent agreement with the quantum mechanical numerical results and can explain well the experimental data of Nelsen *et al.*

I-E-3 Semiclassical Theory of Electron Transfer Beyond the Perturbation Theory

ZHAO, Yi[1]; LIANG, Wanzhen[2]; NAKAMURA, Hiroki
([1]IMS and Univ. Sci. Tech. China, China; [2]Univ. Sci. Tech. China, China)

We consider a problem of evaluating electron transfer rate in the crossover region from nonadiabatic to adiabatic regime controlled by the electron coupling. Based on the generalized nonadiabatic transition state theory1) proposed to overcome the quantitative deficiencies of the conventional transition state theory, the rate applicable to multi-dimensional systems in the linear response limit is expressed as a product of the well-known Marcus formula and a coefficient which represents the correction with respect to nonadiabatic transition across the seam surface. In the case of general multi-dimensional systems the Monte Carlo approach can be utilized to evaluate the effective probability and the effective free energy for any general Hamiltonian system expressed in Cartesian coordinates with nonlinear reaction coordinates and the non-Condon effect taken into account. Numerical demonstration is made by using a model system with a collection of harmonic oscillators. The rate obtained shows a good agreement with that evaluated from the Fermi Gordon rule in the weak electronic coupling limit; while the latter theory fails in the strong electronic coupling regime as expected. Numerical tests also show that a matching technique from multi-mode to an effective one mode gives a very good result in wide range of electronic coupling strength and temperature except in the deep tunneling regime.

Reference

1) Y. Zhao, G.V. Mil'nikov and H. Nakamura, *J. Chem. Phys.* **121**, 8854 (2004).

I-E-4 Generalized Trajectory Surface Hopping Approach

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

The TSH method is generalized so as to be applicable to high dimensional systems with use of the Zhu-Nakamura formulas. Not only the classically allowed transitions but also the classically forbidden ones can be treated uniformly. Furthermore the transition direction can be determined from the Hessian of potential energy surfaces, even if the nonadiabatic coupling vector is not available.

I-E-5 Semiclassical Theory of Thermal Rate Constant for Multi-Surface Processes

CHIKAZUMI, Shinpei; MIL'NIKOV, Gennady V.; NAKAMURA, Hiroki

A semiclassical theory is formulated with use of the Zhu-Nakamura theory by extending the trace formula devised by Miller and co-workers. The statistical Monte Carlo method makes it possible to apply this theory to multi-dimensional systems.

I-F Theory of Nonadiabatic Transition

I-F-1 Rabi Dynamics of Coupled Atomic and Molecular Bose-Einstein Condensates

ISHKHANYAN, Artur[1]; CHERNIKOV, G. P.[2]; NAKAMURA, Hiroki
([1]IMS and Engineering Cent. Armenian NAS, Armenia; [2]Russian Res. Cent. "Kurchatov Institute," Inst. Nuclear Fusion, Russia)

[*Phys. Rev. A* **70**, 053611 (2004)]

The dynamics of coherent Rabi oscillations in coupled atomic and molecular Bose-Einstein condensates is considered taking into account the atom-atom, atom-molecule and molecule-molecule elastic interactions. The exact solution for the molecule formation probability is derived in terms of the elliptic functions. The two-dimensional space of the involved parameters (intensity and detuning) is analyzed and divided into two regions where the Rabi oscillations show different characteristics. A resonance curve is found, on which the molecular formation probability monotonically increases as a function of time. The maximum value of the final transition probability on this curve is 1/2 (*i.e.*, total transition to the molecular state) and it is achieved at high field intensities starting from a minimal threshold defined by the interspecies interaction scattering lengths. The explicit form of the resonance curve is determined, and it is shown that the resonance frequency position reveals a nonlinear dependence on the Rabi frequency of the applied field. A singular point is found on the resonance curve, where a power-law time evolution of the system is observed.

I-F-2 A Basic Two-State Model for Bosonic Field Theories with a Cubic Nonlinearity

ISHKHANYAN, Artur[1]; JAVANAINEN, Juha[2]; NAKAMURA, Hiroki
([1]IMS and Engineering Cent. Armenian NAS, Armenia; [2]Univ. Connecticut, U.S.A.)

[*J. Phys. A: Math. Gen.* **38**, 3505–3516 (2005)]

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

I-F-3 Incorporation of Nonadiabatic Transition into Wave Packet Dynamics

MIL'NIKOV, Gennady V.; ZOU, Shiyang[1]; NAKAMURA, Hiroki
([1]IMS and Univ. Bristol, U.K.)

Non-adiabatic wave packet dynamics is factorized into purely adiabatic propagation and instantaneous localized non-adiabatic transition. A general formula is derived for the quantum mechanical local non-adiabatic operator which is implemented within the framework of R-matrix method. The operator can be used for incorporating the nonadiabatic transition in semclassical wave packets dynamics.

I-G Theory of Multi-Dimensional Tunneling

I-G-1 Instanton Theory for the Tunneling Splitting of Low Vibrationally Excited States

MIL'NIKOV, Gennady V.; NAKAMURA, Hiroki

[*J. Chem. Phys.* **122**, 124311 (2005)]

We develop the instanton theory for calculating the tunneling splitting of excited states. For the case of low vibrational quantum states we derive a canonically invariant formula which is applicable to a multidimensional system of arbitrary Riemannian metric. The effect of multidimensionality in relation to the vibrational excitation is explained in terms of the effective frequencies along the instanton trajectory. The theory is demonstrated to work well by taking HO_2 molecule as an example.

I-G-2 Effect of Out-Of Plane Vibration on the Hydrogen Atom Transfer Reaction in Malonaldehyde

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

[*Chem. Phys. Lett.* **397**, 435–440 (2004)]

Tunneling splitting of the vibrational ground state is calculated for a planar model of malonaldehyde by the instanton method of Mil'nikov and Nakamura with use of *ab initio* potential energy surface. The planar model gives much larger tunneling splitting than the previous full dimensional calculations, indicating a strong effect of the anharmonic coupling between the in-plane and out-of-plane modes. The anharmonicity is related to the Coriolis coupling between the OH stretching vibration and the pseudo-rotation of the hindered rotor. The present results suggest that the multidimensional effects should be carefully taken into account in the tunneling dynamics of polyatomic molecules.

I-G-3 Ground State and Vibrationally Assisted Tunneling in the Formic Acid Dimer

MIL'NIKOV, Gennady V.; KÜHN, O.[1]; NAKAMURA, Hiroki
([1]Freie Univ. Berlin, Germany)

[*J. Chem. Phys.* **123**, 074308 (2005)]

The previously developed instanton theory1) is applied to the calculation of vibrationally assisted tunneling splitting of the deuterated formic acid dimer $(DCOOH)_2$ with all the degrees of freedom taken into account. The ground state tunnel splitting is determined by the density functional theory combined with coupled cluster level of quantum chemistry to be 0.0038 cm^{-1} which is comparable to the experimental value 0.0029 cm^{-1}. Further, the tunnel splittings of fundamental excitations are estimated for frequencies below 300 cm^{-1}. In this energy range it is found that the excitation modes may either enhance or suppress tunneling as compared to the ground state. For the higher frequency modes a rapid growth of the tunnel splitting is observed. At frequencies above 1000 cm^{-1} the semiclassical solution becomes unstable and no reliable tunneling splittings can be obtained. This is in vast contrast to the adiabatic approximation to the instanton theory in which the tunnel splittings can be retrieved up to 3000 cm^{-1}. We discuss this disparity from the viewpoint of the multidimensional character of tunneling in hydrogen bonds and the adiabatic approximation is concluded to be inaccurate.

Reference

1) *J. Chem. Phys.* **122**, 124311 (2005).

I-H Laser Control of Molecular Processes

I-H-1 Laser Control of Electronic Transitions of Wave Packet by Using Quadratically Chirped Pulses

ZOU, Shiyang[1]; KONDORSKIY, Alexey; MIL'NIKOV, Gennady V.; NAKAMURA, Hiroki
([1]IMS and Univ. Bristol, U.K.)

[*J. Chem. Phys.* **122**, 084112 (2005)]

An effective scheme is proposed for the laser control of wave packet dynamics. It is demonstrated that by using specially designed quadratically chirped pulses, fast and nearly complete excitation of wave packet can be achieved without significant distortion of its sharpe. The parameters of the laser pulse can be estimated analytically from the Zhu-Nakamura theory of nonadiabatic transition. If the wave packet is not too narrow or not too broad, then the scheme is expected to be utilizable for multidimensional systems. The scheme is applicable to various processes such as simple electronic excitation, pump-dump, and selective bond breaking, and it is actually numerically demonstrated to work well by taking diatomic and triatomic molecules (LiH, NaK, H_2O) as examples.

I-H-2 Semiclassical Guided Optimal Control of Molecular Dynamics

KONDORSKIY, Alexey; MIL'NIKOV, Gennady V.; NAKAMURA, Hiroki

An efficient semiclassical optimal control theory applicable to multi-dimensional systems is formulated for controlling wave packet dynamics on a single adiabatic potential energy surface. The approach combines advantages of different formulations of optimal control theory: quatntum and classical on one hand and global and local on the other. Numerical applications to the control of NCH-HNC isomerization demonstrate that this theory can provide an efficient tool to manipulate molecular dynamics of many degrees of freedom by laser pulses.

I-I Development of New Molecular Functions

I-I-1 A Theoretical Study of Cyclohexadiene/Hexatriene Photochemical Interconversion: Miltireference Configuration Interaction Potential Energy Surfaces and Transition Probabilities for the Radiationless Decays

TAMURA, Hiroyuki; NANBU, Shinkoh[1]; NAKAMURA, Hiroki; ISHIDA, Toshimasa[2]
([1]IMS and Kyushu Univ.; [2]IMS and Kyoto Univ.)

[*Chem. Phys. Lett.* **401**, 487–491 (2005)]

The overall energetics and the feature of reactive potential energy surfaces for the photochemical interconversion between cyclohaxadiene (CHD) and all-*cis*-hexatriene (cZc-HT) have been investigated using the multireference configuration interaction (MRCI) calculations. The adiabatic and the diabatic potential energy surfaces of the ground and the excited states have been calculated along the Jacobi coordinates. The conical intersections among the states are estimated and the corresponding non-adiabatic transition probabilities are calculated using the semiclassical Zhu-Nakamura formula. The 1^1B-2^1-A decay occurs by C_2-symmetry-breaking motion around the conical intersection. The non-adiabatic transition to 1^1A occurs by the motion toward the 5-menbered ring.

I-I-2 Reaction Dynamics of Cyclohexadiene/Hexatriene Ultrafast Photoisomerization through Conical Intersections

TAMURA, Hiroyuki; NANBU, Shinkoh[1]; ISHIDA, Toshimasa[2]; NAKAMURA, Hiroki
([1]IMS and Kyushu Univ.; [2]IMS and Kyoto Univ.)

Fundamental mechanisms of photochromism applicable to molecular switches and memories are clarified using quantum mechanical wave-packet dynamics on the accurate *ab initio* potential energy surfaces. Cyclohexadiene/hexatriene ultrafast photoisomerization has been considered as a model system. The results are in agreement with the femtosecond time-resolution experiments. The overall reaction dynamics is revealed from photoexcitation to the ground state products *via* non-adiabatic transitions through conical intersections governing the excited state lifetime and the reaction yield. It is also found that the second excited state plays an important role in the dynamics and the efficiency of photochromism.

I-I-3 Encapsulation of Hydrogen Atoms by Fullerenes and Carbon Nanotubes with the Use of Nonadiabatic Transition

NANBU, Shinkoh[1]; ISHIDA, Toshimasa[2]; NAKAMURA, Hiroki
([1]IMS and Kyushu Univ.; [2]IMS and Kyoto Univ.)

A probable mechanism is proposed to encapsulate hydrogen atoms into carbon nanotubes (CNTs) as well as fullerenes. In this mechanism, a non-adiabatic effect on nuclear dynamics, specifically the non-adiabatic tunneling effect, enables transmission of hydrogen atoms. A cap of CNTs or a pentagonal moiety (five-membered rings) of fullerenes is mimicked by corannulene molecule ($C_{20}H_{10}$). The three-dimensional quantum mechanical wave packet dynamics calculations are carried out on the accurate ab initio potential energy surfaces of the ground and excited states. It is shown that a hydrogen atom can transmit through the five-membered ring of corannulene more than once out of four incidences when five carbon atoms in the second layer are replaced by borons. The result is interpreted in terms of the Zhu-Nakamura semiclassical theory of non-adiabatic transition.

I-J Theoretical Studies of Electron Dynamics in Molecular Systems

Electron dynamics in molecular systems is an intrinsic process related to a number of interesting phenomena such as linear and nonlinear optical response, electric conduction, and also chemical reaction. Despite the importance, the electron dynamics has not been understood in detail. We have developed a computational method simulating the electron dynamics in real time, and investigated nonlinear optical response and multiple ionization of noble metal clusters.

I-J-1 High-Order Harmonic Generation from Silver Clusters: Laser-Frequency Dependence and the Screening Effect of *d* Electrons

NOBUSADA, Katsuyuki; YABANA, Kazuhiro[1]
([1]Univ. Tsukuba)

[*Phys. Rev. A* **70**, 043411 (7 pages) (2004)]

We present time-dependent density functional studies of harmonic generation from Ag_2 and Ag_8 in pulsed laser fields. The harmonic generation is strongly dependent on the laser frequency. The harmonics are emitted from the clusters much more efficiently when the applied laser field is in tune with the dipole resonance frequency of the system. Such resonance frequency dependence is substantially equal to a resonance phenomenon in a forced oscillator in a sense that the valence *s*-electrons are shaken effectively at the tuned laser frequency and the induced dipole moment continues to oscillate even though the laser field is switched off. Furthermore, we have found that the polarizable core *d*-electrons significantly screen the valence *s*-electrons such that the electron density of the *s* electrons induced in the laser field is canceled out. The screening effect of the *d* electrons becomes more important in the system of Ag_8 than Ag_2.

I-J-2 Multiple Ionization of a Silver Diatomic Molecule in an Intense Laser Field

SHIRATORI, Kazuya[1]; NOBUSADA, Katsuyuki; YABANA, Kazuhiro[2]
([1]Hokkaido Univ.; [2]Univ. Tsukuba)

[*Chem. Phys. Lett.* **404**, 365–369 (2005)]

Time-dependent density functional studies of multiple ionization of Ag_2 in an intense laser field 10^{14} W/cm^2 are presented. Special emphasis is placed on elucidating frequency dependence and effects of the *d* electrons on the ionization processes. We have found that the *s* and *d* electrons move reciprocally toward the opposite directions in a manner such that the electric field induced by the *s*-electron polarization is cancelled out by the *d* electrons. This screening effect of the *d* electrons suppresses the multiple ionization in marked contrast to molecular systems such as alkali metal clusters which do not accompany inner *d*-electrons.

I-K Electronic Structures and Photochemical Properties of Nanometer-Sized Metal Clusters

Nanometer-sized metal clusters provide significantly different physicochemical properties such as optical response, catalysis, and reactivity from corresponding bare metal clusters or bulk metals. We have investigated electronic structures and photochemical properties of monolayer-protected metal clusters with special emphasis on describing metal-molecule interactions.

I-K-1 Electronic Structure and Photochemical Properties of a Monolayer-Protected Gold Cluster

NOBUSADA, Katsuyuki

[*J. Phys. Chem. B* **108**, 11904–11908 (2004)]

The electronic structure of a monolayer-protected gold cluster, $[Au_{13}(SCH_3)_8]^{3+}$, has been investigated by performing density functional calculations. The cluster has a characteristic structure with O_h molecular symmetry and eight (111) facets of a centered cuboctahedral Au_{13} core cluster are fully passivated by eight methanethiolates. The bond distance between two neighboring gold atoms (= 3.673 Å) is much larger than that of the bare Au_{13} cluster (= 2.929 Å), whereas the Au–S bond distance is 2.403 Å. These atomic rearrangement means that the methanethiolates stabilize the enlarged bare Au_{13} cluster by bonding to the (111) hollow sites of the bare cluster. The absorption spectrum of the $[Au_{13}(SCH_3)_8]^{3+}$ cluster is simulated within time-dependent density functional theory. The spectrum shows clear absorption peaks and each peak is assigned to specific excitation processes.

I-K-2 Glutathione-Protected Gold Clusters Revisited: Bridging the Gap between Gold(I)-Thiolate Complexes and Thiolate-Protected Gold Nanocrystals

NEGISHI, Yuichi; NOBUSADA, Katsuyuki; TSUKUDA, Tatsuya

[*J. Am. Chem. Soc.* **127**, 5261–5270 (2005)]

Small gold clusters (~1 nm) protected by molecules of a tripeptide, glutathione (GSH), were prepared by reductive decomposition of Au(I)-SG polymers at a low temperature and separated into a number of fractions by polyacrylamide gel electrophoresis (PAGE). Chemical compositions of the fractionated clusters determined previously by electrospray ionization (ESI) mass spectrometry (Negishi, Y. *et al.*, *J. Am. Chem. Soc.* **126**, 6518 (2004)) were reassessed by taking advantage of freshly prepared samples, higher mass resolution, and more accurate mass calibration; the nine smallest components are reassigned to $Au_{10}(SG)_{10}$, $Au_{15}(SG)_{13}$, $Au_{18}(SG)_{14}$, $Au_{22}(SG)_{16}$, $Au_{22}(SG)_{17}$, $Au_{25}(SG)_{18}$, $Au_{29}(SG)_{20}$, $Au_{33}(SG)_{22}$, and $Au_{39}(SG)_{24}$. These assignments were further confirmed by measuring the mass spectra of the isolated Au:S(h-G) clusters, where h-GSH is a homoglutathione. It is proposed that a series of the isolated Au:SG clusters corresponds to kinetically trapped intermediates of the growing Au cores. The relative abundance of the isolated clusters was correlated well with the thermodynamic stabilities against unimolecular decomposition. The electronic structures of the isolated Au:SG clusters were probed by X-ray photoelectron spectroscopy (XPS) and optical spectroscopy. The Au(4f) XPS spectra illustrate substantial electron donation from the gold cores to the GS ligands in the Au:SG clusters. The optical absorption and photoluminescence spectra indicate that the electronic structures of the Au:SG clusters are well quantized; embryos of the sp band of the bulk gold evolve remarkably depending on the number of the gold atoms and GS ligands. The comparison of these spectral data with those of sodium Au(I) thiomalate and 1.8 nm Au:SG nanocrystals (NCs) reveals that the subnanometer-sized Au clusters thiolated constitute a distinct class of binary system which lies between the Au(I)-thiolate complexes and thiolate-protected Au NCs.

I-K-3 Gold-Thiolate Nanoring: Electronic Structure and Photochemical Properties

NOBUSADA, Katsuyuki

We have studied electronic structure and photochemical properties of gold-methanethiolate complexes $Au_n(SCH_3)_n$. The complexes have been found to be stable structures in the form of a circular ring. The characteristic Au–S interaction plays an important role in forming such a unique ring structure. The ring structure also provides interesting photochemical properties which are rather different from those of similar-sized gold-methanethiolate clusters.

I-L 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. About 15 years ago, we have proposed a 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 method was applied successfully to a variety of chemical processes in solution including a number of different types of chemical reactions, S_N2, acid-base, redox, and so on.

More recently, we have revised the theory so that the theory can account for the three dimensional distribution of solvent around solute.[2)] (3D-RISM) This revision turns out to be essential when one tries to treat the solvent distribution around the native state of protein. The new theory allows us to handle the electronic structure of protein in water with appropriate theories for quantum chemistry.

References

1) S. Ten-no, F. Hirata and S. Kato, *Chem. Phys. Lett.* **214**, 391 (1993); *J. Chem. Phys.* **100**, 7443 (1994); H. Sato, F. Hirata and S. Kato, *J. Chem. Phys.* **105**, 1546 (1996).
2) H. Sato, A. Kovalenko and F. Hirata, *J. Chem. Phys.* **112**, 9463 (2000).

I-L-1 Electronic Structure Calculation of a Solvated Macro Molecule by Using Three-Dimensional Reference Interaction Site Model Combined with *Ab Initio* Molecular Orbital Theory

YOSHIDA, Norio; HIRATA, Fumio

[*J. Comput. Chem.* submitted]

The three dimensional reference interaction site model integral equation theory (3D-RISM) combined with the *ab initio* molecular orbital method (3D-RISM-SCF) is applied to a solvated macro molecular system.

The solvation structure around a solute molecule is obtained from the 3D-RISM integral equation under the electrostatic potential of the solute molecule, calculated by the *ab initio* molecular orbital theory.

The electrostatic potential should be calculated on each grid point in the three dimensional real space. Hence the solvated fock matrix are also prepared on each grid point. Therefore, the calculation of the electrostatic potential and the solvated fock matrix is the most time consuming part in this method. In this paper, we propose a new procedure to save the computational cost for calculating the electrostatic potential and the solvated fock matrix. The strategy of this procedure is to divide the space into three regions: (I) the inside of the repulsive cores, and (II) the region excluding(I), where the electron density is distributed, and (III) the remaining part in the super cell after applying the (I) and (II).

In the first region, it is possible to avoid the calculation of electrostatic potential and solvated Fock matrix by assuming the potential to be infinity.

In the second region, the electrostatic potential is evaluated directly by integrating the molecular orbitals. In the outermost region, it is evaluated approximately by putting the effective point charge on each atomic site.

The electronic structure and the energy gradient of Methionine-Enkephalin and solvation structure are estimated by using this procedure in aqueous solution, and are compared with the results from other procedures. The results are compared also with those from the continuum model.

I-L-2 New Theoretical Approach for the Diastereoselectivity of H/D Exchange Reaction on Methyl 3-Fluorobutanoate Anion

IKUTA, Yasuhiro; YOSHIDA, Norio; YAMAZAKI, Takeshi[1]; HIRATA, Fumio
([1]NINT, Canada)

[*Tetrahedron Lett.* submitted]

The origin of closed to si-face stereochemistry in the protonation of β-substituted ethyl butanoates in ethanol-*d*, which has been studied by Mohrig and co-workers, was examined with Me 3-fluoro butanoate anion as a computational model. It was found that the prediction of the selectivity was achieved with the solvent effect arround substrate and the population fo the ground state species. The transition state to si-face streochemistry is found to be the most favorable process in ethanol.

I-M 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.

In the past 10 years, we have been developing a method to attack the problem based on the statistical mechanics of liquids, especially, on the RISM theory.[1)] Recently, we put forward our effort to apply the three dimensional (3D) RISM theory to biomolecules, and have succeeded for the first time to obtain thermodynamic quantities of "real" protein, which is in agreement with experiments not only qualitatively but also quantitatively in case of the partial molar volume.[2)] The 3D-RISM theory turns out to be even more powerful to explore water molecules trapped in a cavity of protein.

References
1) M. Kinoshita, Y. Okamoto and F. Hirata, *J. Am. Chem. Soc.* **120**, 1855 (1998).
2) T. Imai, A. Kovalenko and F. Hirata, *Chem. Phys. Lett.* **395**, 1 (2004).

I-M-1 Hydrophobic Effects on Partial Molar Volume

IMAI, Takashi[1]; HIRATA, Fumio
([1]Ritsumeikan Univ.)

[*J. Chem. Phys.* **122**, 94509 (2005)]

The hydrophobic effects on partial molar volume (PMV) are investigated as a PMV change in the transfer of a benzene-like non-polar solute from the non-polar solvent to water, using an integral equation theory of liquids.

The volume change is divided into two effects. One is the "packing" effect in the transfer from the non-polar solvent to hypothetical "non-polar water" without hydrogen bonding networks. The other is the "iceberg" effect in the transfer from "non-polar water" to water. The results indicate that the "packing" effect is negative and a half compensated by the positive "iceberg" effect. The "packing" effect is explained by the difference in the solvent-compressibility. Further investigation shows that the sign and magnitude of the volume change depends on the solute-size and the solvent-compressibility. The finding gives a significant implication that the exposure of a hydrophobic residue caused by protein denaturation can either increase or decrease the PMV of protein depending on the size of the residue and the fluctuation of its surroundings. Possible applications of the method to problems related to the solvation thermodynamics of protein are discussed.

I-M-2 Partial Molar Volume of Proteins Studied by the 3D-RISM Theory

IMAI, Takashi[1]; KOVALENKO, Andriy[2]; HIRATA, Fumio
([1]Ritsumeikan Univ.; [2]NINT, Canada)

[*J. Phys. Chem. B* **109**, 6658 (2005)]

The three-dimensional reference interaction site model (3D-RISM) theory is applied to the analysis of hydration effects on the partial molar volume of proteins. For the native structure of some proteins, the partial molar volume is decomposed into geometric and hydration contributions using the 3D-RISM theory combined with the geometric volume calculation.

The hydration contributions are correlated with the surface properties of protein. The thermal volume, which is the volume of voids around the protein induced by the thermal fluctuation of water molecules, is directly proportional to the accessible surface area of protein. The interaction volume, which is the contribution of electrostatic interactions between the protein and water molecules, is apparently governed by the charged atomic groups on the protein surface. The polar atomic groups does not make any contribution to the interaction volume. The volume differences between low- and high-pressure structures of lysozyme are also analyzed by the present method.

I-M-3 Theoretical Study of Volume Changes Associated with the Helix-Coil Transition of an Alanine-Rich Peptide in Aqueous Solution

IMAI, Takashi[1]; TAKEKIYO, Takahiro[1]; KOVALENKO, Andriy[2]; HIRATA, Fumio; TANIGUCHI, Yoshihiro[1]
([1]Ritsumeikan Univ.; [2]NINT, Canada)

The changes in the partial molar volume (PMV) associated with the conformational transition of an alanine-rich peptide AK16 from the α-helix structure to various random coil structures are calculated by the three-dimensional interaction site model (3D-RISM) theory coupled with the Kirkwood-Buff theory. The volume change is analyzed by decomposing it into contributions from geometry and hydration: the changes in the van der Waals, void, thermal, and interaction volume. The total change in the PMV is positive. This is primarily due to the growth of void space within the peptide which is cancelled in part by the volume reduction resulting from the increase in the electrostatic interaction between the peptide and water molecules. The changes in the void and thermal volume of the coil structures are widely distributed and tend to compensate each other. Additionally, the relations between the hydration volume components and the surface properties are investigated. We categorize coil structures into extended coils with the PMV smaller than helix and general coils with the PMV larger than helix. The pressure therefore can both stabilize and destabilize the coil structures. The latter seems to be a more proper model of random coil structures of the peptide.

I-M-4 Combination of the Replica-Exchange Monte Carlo Method and the Reference Interaction Site Model Theory for Simulating a Peptide Molecule in Aqueous Solution

MITSUTAKE, Ayori[1]; KINOSHITA, Masahiro[2]; OKAMOTO, Yuko[3]; HIRATA, Fumio
([1]Keio Univ.; [2]Kyoto Univ.; [3]Nagoya Univ.)

[*J. Phys. Chem. B* **108**, 19002 (2004)]

This article reports the first attempt to combine the replica-exchange Monte Carlo method and the reference interaction site model (RISM) theory for simulating a peptide molecule in aqueous solution. The energy function is the sum of the conformational energy and the solvation free energy. The solvation free energy for a fixed conformation of the peptide molecule is calculated using the RISM theory. The replica-exchange method is modified so that the dependence of the energy function on the temperature can be incorporated. The effectiveness of the combined approach is demonstrated for Met-enkephalin in water. It is argued that the number of replicas required for a peptide molecule immersed in water is drastically reduced by emplying the combined approach. Solvation properties and free energy surfaces of Met-enkephalin in water are discussed.

I-M-5 Water Molecules in a Protein Cavity Detected by a Statistical-Mechanical Theory

IMAI, Takashi[1]; HIRAOKA, Ryusuke[1]; KOVALENKO, Andriy[2]; HIRATA, Fumio
([1]Ritsumeikan Univ.; [2]NINT, Canada)

[*J. Am. Chem. Soc. communication*, submitted]

Water molecules confined inside cavities in a protein are of great importance in understanding the structure, stability, and functions of the biomolecule. Considerable efforts have been devoted to observe such water molecules by experiments, but it is still a nontrivial task.

It is virtually impossible to “find” water molecules in a protein cavity by the ordinary molecular simulation, because they are most likely trapped in the biomolecule through a process of large conformational fluctuation or “folding.” The simulation of such water molecules is as difficult as the protein folding itself.

Surprisingly enough, in the present study, we could have detected water molecules in a protein cavity by means of a recently developed statistical mechanics of molecular solutions, or the three-dimensional reference interaction site model (3D-RISM) theory. This paper reports how the water molecules are detected by the 3D-RISM calculation.

The results may have great impact on biochemistry and biophysics including molecular recognition, enzymatic reaction, and so on.

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

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

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

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

I-N-1 Site-Site Memory Equation Approach in Study of Density/Pressure Dependence of Translational Diffusion Coefficient and Rotational Relaxation Time of Polar Molecular Solutions: Acetonitrile in Water, Methanol in Water, and Methanol in Acetonitrile

KOBRYN, Alexander; YAMAGUCHI, Tsuyoshi[1]; HIRATA, Fumio
([1]Nagoya Univ.)

[*J. Chem. Phys.* **122**, 184511 (2005)]

We present results of theoretical study and numerical calculation of the dynamics of molecular liquids based on combination of the memory equation formalism and the reference interaction site model—RISM. Memory equations for the site-site intermediate scattering functions are studied in the mode-coupling approximation for the first order memory kernels, while equilibrium properties such as site-site static structure factors are deduced from RISM. The results include the temperature-density(pressure) dependence of translational diffusion coefficients D and orientational relaxation times τ for acetonitrile in water, methanol in water and methanol in acetonitrile, all in the limit of infinite dilution. Calculations are performed over the range of temperatures and densities employing the SPC/E model for water and optimized site-site potentials for acetonitrile and methanol. The theory is able to reproduce qualitatively all main features of temperature and density dependences of D and τ observed in real and computer experiments. In particular, anomalous behavior, *i.e.* the increase in mobility with density, is observed for D and τ of methanol in water, while acetonitrile in water and methanol in acetonitrile do not show deviations from the ordinary behavior. The variety exhibited by the different solute-solvent systems in the density dependence of the mobility is interpreted in terms of the two competing origins of friction, which interplay with each other as density increases: the collisional and dielectric frictions which, respectively increase and decrease with increasing density.

I-N-2 Theoretical Study on the Dynamic Properties of Compressed Water and Water-Hydrophobic Solute Mixtures

YAMAGUCHI, Tsuyoshi[1]; MATSUOKA, Tatsuro[1]; KODA, Shinobu[1]; CHONG, Song-Ho; HIRATA, Fumio
([1]Nagoya Univ.)

The dynamic properties, including shear viscosity, self-diffusion coefficient, dielectric relaxation time and single-molecular reorientational relaxation time, of neat compressed water and model water-hydrophobic solute mixtures are calculated theoretically from the intermolecular interaction potentials. The reference interaction-site model integral equation theory is used to obtain the equilibrium structure of the liquid, which in turn is used as the input of the numerical calculation by the mode-coupling theory for molecular liquids based on the interaction-site model. For neat compressed water, the theory reproduced the increase in the molecular mobility with applying pressure qualitatively. The reorientational mobility is more enhanced by pressure than the translational one, which is in harmony with experiments. The retardation of the motion of water in the aqueous solution of hydrophobic solutes is also obtained by the theory. In a model system in which the electrostatic interaction between the solute and solvent is continuously varied, the mobility of solvent water has a maximum as the function of the hydrophobicity of the solute. This theoretical trend is in harmony with the transition from positive, *via* negative, to hydrophobic hydration regimes experimentally observed.

I-N-3 Solvation Dynamics in Water Investigated by RISM/Mode-Coupling Theory

NISHIYAMA, Katsura[1]; YAMAGUCHI, Tsuyoshi[2]; HIRATA, Fumio; OKADA, Tadashi[1]
([1]Osaka Univ.; [2]Nagoya Univ.)

[*J. Mol. Liq.* **119**, 63 (2005)]

The reference interaction site model (RISM) theory combined with the generalized Langevin/mode-coupling theory (MCT) is applied to the investigation of solvation dynamics in water. The dynamic response function Ss(t) which measures the energy relaxation of the system is calculated with different model solutes. The RISM-MCT framework recently presented by Yamaguchi and coworkers [*J. Chem. Phys.* **117**, 2216 (2002); *Mol. Phys.* **101**, 1211 (2003)] is shown to be applicable well to the realistic description of solvation dynamics. Ss(t) initially relaxes with a Gaussian decay followed by an overdamping oscillation with the time period of 30 fs. As the multiplicity of the solute pole is increased, the magnitude of the Ss(t) damping becomes smaller and relaxation gets slower.

I-O Statistical Mechanics of Interfacial Fluids

Microscopic structure of fluid interfaces has been drawing a lot of attention due to recent development in the experimental techniques devised particularly to probe the interface. However, there are many open questions remained unanswered. For example, how wide is the interfacial region, how does it depend on the chemical species consisting the solution? Is the interface more or less homogeneous in terms of density or concentration of the two fluids, or is it spatially inhomogeneous? If it is inhomogeneous, what is the spatial extent of the inhomogeneity? Answering those questions is the most difficult and challenging tasks for theoretical physics and chemistry, and not much progress has been made in the past, especially from a molecular view point. We have been developing statistical mechanics for two different types of interfacial fluids: fluid-fluid interface and fluids in porous media. Following are the latest achievement in that direction.

I-O-1 A Molecular Theory of Liquid Interfaces

KOVALENKO, Andriy[1]; HIRATA, Fumio
([1]NINT, Canada)

[*Phys. Chem. Chem. Phys.* **7**, 1785 (2005)]

We propose a site-site generalization of the Lovett-Mow-Buff-Wertheim integro-differential equation for the one-particle density distributions to polyatomic fluids. The method provides microscopic description of liquid interfaces of molecular fluids and solutions. It uses the inhomogeneous site-site direct correlation function of molecular fluid consistently constructed by nonlinear interpolation between the homogeneous ones. The site-site correlations of the coexisting bulk phases are obtained from the reference interaction site model (RISM) integral equation with our closure approximation. For illustration, we calculated the structure of the planar liquid-vapor as well as liquid-liquid interfaces of n-hexane and methanol at ambient conditions.

I-P Photoinduced Phase Transitions in Molecular Materials

Photoirradiation may create electrons, holes or excitons, which are often accompanied by local structural deformation. Sometimes it causes spatially large structural transformations with the help of cooperativity possessed by interacting electrons and molecules. Thus, a nonequilibrium phase can be generated, which may not be reached by simply changing temperature or pressure because the energy of a photon is much higher than thermal energies. Such photoinduced phase transitions have been studied extensively, both experimentally and theoretically. Thanks to the great progress in laser spectroscopy techniques, charge and lattice dynamics are being clarified in many molecular materials on different time scales including ultrafast and/or coherent dynamics. We need to treat relevant itinerant-electron models, whose transfer integrals are off-diagonal elements giving transition amplitudes. This is in contrast to stochastic dynamics in classical statistical models, where transition probabilities are determined by the Boltzmann factors at finite temperatures.

I-P-1 Photoinduced Dynamics and Nonequilibrium Characteristics in Quasi-One-Dimensional Electron Systems: Mott Insulators *vs.* Band Insulators

YONEMITSU, Kenji

[*J. Phys.: Conf. Series* **21**, 30–37 (2005)]

Electron-electron interactions play an important role in nonequilibrium properties of molecular materials. First, we show differences between photoinduced ionic-to-neutral and neutral-to-ionic transitions in quasi-one-dimensional extended Peierls Hubbard models with alternating potentials. Cooperative dynamics lead to nonlinear ionicity in the former, while uncooperative dynamics lead to quite linear ionicity in the latter, as a function of the energy supplied from the oscillating electric field. Interchain electron-electron interactions bring about initial competition among metastable and stable domains in neighboring chains, slowing down the phase transition. Interchain elastic couplings are necessary to form a ferroelectric long-range order. Second, we show differences between field-effect characteristics of Mott insulators and those of band insulators in one-dimensional Hubbard models, to which tight-binding models are attached for metallic electrodes and scalar potentials are added for interfacial barriers. Ambipolar characteristics are found in the former, while unipolar characteristics generally appear in the latter. In the former, charge transport is cooperative so that the drain current is insensitive to the difference between the work function of the channel and that of the electrodes, and thus insensitive to the polarity of the gate bias.

I-P-2 Optical Responses of Photoexcited States in the One-Dimensional Ionic Hubbard Model

MAESHIMA, Nobuya[1]; YONEMITSU, Kenji
([1]IMS and Tohoku Univ..)

[*J. Phys.: Conf. Series* **21**, 183–188 (2005)]

Photoinduced optical responses are studied in the one-dimensional ionic Hubbard model with the nearest-neighbor repulsion V. For $V = 0$, carriers introduced by photoirradiation move freely both in the Mott insulator phase and in the band insulator phase, giving rise to a Drude peak in the optical conductivity spectrum. The carriers in the Mott insulator phase remain conducting for $0 < V < 2t$ because their kinetic energy overcomes the binding energy. By contrast, the electrons and the holes in the band insulator phase are bound to form excitons for $V > 0$, which do not contribute to the charge transport unless the excitation energy allows them to be separated. The dependence of the Drude weight in the lowest-energy photoexcited state on V and the system size is investigated for both phases. Implications to experimental studies of halogen-bridged metal-complex chains are discussed.

I-P-3 Quantum Ising Model Coupled with Conducting Electrons

YAMASHITA, Yasufumi; YONEMITSU, Kenji

[*J. Phys.: Conf. Series* **21**, 232–236 (2005)]

The effect of photo-doping on the quantum paraelectric $SrTiO_3$ is studied by using the one-dimensional quantum Ising model, where the Ising spin describes the effective lattice polarization of an optical phonon. Two types of electron-phonon couplings are introduced through the modulation of transfer integral *via* lattice deformations. After the exact diagonalization and the perturbation studies, we find that photo-induced low-density carriers can drastically alter quantum fluctuations when the system locates near the quantum critical point between the quantum paraelectric and ferroelectric phases.

I-P-4 Photoinduced Metallic Properties of One-Dimensional Strongly Correlated Electron Systems

MAESHIMA, Nobuya[1]; YONEMITSU, Kenji
([1]IMS and Tohoku Univ.)

[*J. Phys. Soc. Jpn.* **74**, 2671–2674 (2005)]

We study photoinduced optical responses of one-dimensional strongly correlated electron systems. Optical conductivity spectra are calculated for the ground and photoexcited states in a one-dimensional Hubbard model at half filling by the exact diagonalization method. It is found that, in the Mott insulator phase, the photoexcited state has large spectral weights including the Drude weight below the optical gap. As a consequence, the spectral weight above the optical gap is markedly reduced. These results imply that a metallic state is induced by photoexcitation. A comparison between the photoexcited and hole-doped states shows that photoexcitation is similar to chemical doping.

I-P-5 Interchain-Coupling Effects on Photoinduced Neutral-Ionic Transition Dynamics in Mixed-Stack Charge-Transfer Complexes

YONEMITSU, Kenji

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

Effects of interchain electron-electron interactions on the photoinduced ionic-to-neutral and neutral-to-ionic transition dynamics are studied in a quasi-one-dimensional extended Peierls-Hubbard model with alternating potentials for mixed-stack charge-transfer complexes. The ionic-to-neutral transition dynamics depend on the strengths of interchain couplings. For weak couplings, the interchain coherence is destroyed. For strong couplings such as those corresponding to TTF-CA, once neutral domains are nucleated above an increased absorption threshold, they grow spontaneously and cooperatively till the whole system is converted. In contrast, interchain couplings slightly enhance nonlinearity of the otherwise uncooperative neutral-to-ionic transition dynamics.

I-P-6 Theory of Photoinduced Phase Transitions

YONEMITSU, Kenji; NASU, Keiichiro[1]
([1]*KEK*)

[*J. Phys. Soc. Jpn.* in press]

Theories of photoinduced phase transitions have developed along with the progress in experimental studies, especially concerning their nonlinear characters and transition dynamics. At an early stage, stochastic dynamics are explained on the basis of statistical physics. Recently, a variety of dynamics observed in different electronic states are described by relevant electronic models. Especially, coherent motion of a macroscopic domain boundary needs appropriate interactions among electrons and lattice displacements. We describe the history of theories of photoinduced phase transitions and discuss a future perspective.

I-Q Collective Transport through Metal-Insulator Interfaces

Molecular materials are used in many device structures. Charge transport is always through an interface between two materials with different electronic states and work functions. In field-effect transistors fabricated on an insulating material with coherent charge transport under electric fields, the insulator-(source/drain) electrode interface barrier potentials, known as Schottky barriers, play an important role. For band insulators, the Schottky barriers indeed govern the current-voltage characteristics. Because the work function of the electrodes is generally different from that of the material, the characteristics are generally very asymmetric with respect to the polarity of the gate bias and therefore unipolar. Quite recently, ambipolar characteristics are found in field-effect transistor device structures based on organic single crystals of a quasi-one-dimensional Mott insulator. The ambipolar characteristics imply very similar effects on electron and hole injections of the Schottky barriers when combined with electron correlation effects. We need to combine interacting electron models with electrostatic potentials that originate from the long-range Coulomb interaction and are responsible for the interface barrier potentials.

I-Q-1 Mechanism of Ambipolar Field-Effect Carrier Injections in One-Dimensional Mott Insulators

YONEMITSU, Kenji

[*J. Phys. Soc. Jpn.* **74**, 2544–2553 (2005)]

To clarify the mechanism of recently reported, ambipolar carrier injections into quasi-one-dimensional Mott insulators on which field-effect transistors are fabricated, we employ the one-dimensional Hubbard model attached to a tight-binding model for source and drain electrodes. To take account of the formation of Schottky barriers, we add scalar and vector potentials, which satisfy the Poisson equation with boundary values depending on the drain voltage, the gate bias, and the work-function difference. The current-voltage characteristics are obtained by solving the time-dependent Schrödinger equation in the unrestricted Hartree-Fock approximation. Its validity is discussed with the help of the Lanczos method applied to small systems. We find generally ambipolar carrier injections in Mott insulators even if the work function of the crystal is quite different from that of the electrodes. They result from balancing the correlation effect with the barrier effect. For the gate-bias polarity with higher Schottky barriers, the correlation effect is weakened accordingly, owing to collective transport in the one-dimensional correlated electron systems.

I-R Strongly Correlated Electron Systems with Frustrations

Strongly correlated electron systems have produced many exotic phases. Especially in low dimensions, there are always subtle balances between the tendency toward a long-range order through instabilities and the tendency against it due to quantum fluctuations. Geometrical frustrations and/or orbital degrees of freedom enhance quantum fluctuations to lead to intriguing phenomena. Phase diagrams are clarified by paying special attentions to low-energy excitations near quantum critical points.

I-R-1 Frustration-Induced η Inversion in the S = 1/2 Bond-Alternating Spin Chain

MAESHIMA, Nobuya[1]**; OKUNISHI, Kouichi**[2]**;**
OKAMOTO, Kiyomi[3]**; SAKAI, Tôru**[4]
([1]IMS and Tokyo Metropolitan Univ.; [2]Niigata Univ.; [3]Tokyo Inst. Tech.; [4]Tohoku Univ.)

[*Phys. Rev. Lett.* **93**, 127203 (4 pages) (2004)]

We study the frustration-induced enhancement of the incommensurate correlation for a bond-alternating quantum spin chain in a magnetic field, which is associated with a quasi-one-dimensional organic compound F_5PNN. We investigate the temperature dependence of the staggered susceptibilities by using the density matrix renormalization group, and then find that the incommensurate correlation becomes dominant in a certain range of the magnetic field. We also discuss the mechanism of this enhancement on the basis of the mapping to the effective S = 1/2 XXZ chain and a possibility of the field-induced incommensurate long-range order.

I-R-2 Field-Induced Phase Transitions and Long-Range Orders in the S = 1/2 Spin Bond-Alternating Chain with Frustrating Interaction

MAESHIMA, Nobuya[1]**; OKUNISHI, Kouichi**[2]**;**
OKAMOTO, Kiyomi[3]**; SAKAI, Tôru**[4]**;**
YONEMITSU, Kenji
([1]IMS and Tohoku Univ.; [2]Niigata Univ.; [3]Tokyo Inst. Tech.; [4]Tohoku Univ.)

[*J. Phys. Soc. Jpn.* **74**, Suppl. 63–66 (2005)]

We study field-induced phase transitions and long-range orders in the S = 1/2 spin bond-alternating chain with frustrating interaction. By using the inter-chain mean field theory combined with the finite temperature density matrix renormalization group, we investigate properties of field-induced long-range orders and phase transitions. We find that the inter-chain interaction strongly affects the realized phases of this system.

I-R-3 Field-Induced Incommensurate Order in Frustrated Spin Chain

MAESHIMA, Nobuya[1]**; OKUNISHI, Kouichi**[2]**;**
OKAMOTO, Kiyomi[3]**; SAKAI, Tôru**[4]**;**
YONEMITSU, Kenji
([1]IMS and Tohoku Univ.; [2]Niigata Univ.; [3]Tokyo Inst. Tech.; [4]Tohoku Univ.)

[*Prog. Theor. Phys.* submitted]

A mechanism of the incommensurate long-range order induced by external magnetic field is considered to propose its possible realization in the bond-alternating spin chain F_5PNN. Using the density matrix renormalization group analysis, we present several typical phase diagrams, depending on the interchain interaction and the frustration due to the next-nearest-neighbor coupling. A possible magnetization plateau at half the saturation moment is also discussed.

I-R-4 Phase Diagram of the Excitonic Insulator

HÜLSEN, Björn[1]**; BRONOLD, Franz X.**[2]**; FEHSKE, Holger**[2]**; YONEMITSU, Kenji**
([1]Fritz-Haber-Inst.; [2]Ernst-Moritz-Arndt-Univ.)

[*Physica B* in press]

Motivated by recent experiments, which give strong evidence for an excitonic insulating phase in $TmSe_{0.45}Te_{0.55}$, we developed a scheme to quantitatively construct, for generic two-band models, the phase diagram of an excitonic insulator. As a first application of our approach, we calculated the phase diagram for an effective mass two-band model with long-range Coulomb interaction. The shielded potential approximation is used to derive a generalized gap equation controlling for positive (negative) energy gaps the transition from a semi-conducting (semi-metallic) phase to an insulating phase. Numerical results, obtained within the quasi-static approximation, show a steeple-like phase diagram in contrast to long-standing expectations.

I-R-5 Effective Interaction between the Interpenetrating Kagome Lattices in Na_xCoO_2

INDERGAND, Martin[1]**; YAMASHITA, Yasufumi;**
KUSUNOSE, Hiroaki[2]**; SIGRIST, Manfred**[1]
([1]ETH-Hönggerberg; [2]Tohoku Univ.)

[*Phys. Rev. B* **71**, 214414 (19 pages) (2005)]

A multiorbital model for a CoO_2 layer in Na_xCoO_2 is derived. In this model, the kinetic energy for the degenerate t_{2g} orbitals is given by indirect hopping over oxygen, leading naturally to the concept of four interpenetrating Kagome lattices. Local Coulomb interaction couples the four lattices and an effective Hamiltonian for the interaction in the top band can be written in terms of fermionic operators with four different flavors. Focusing on charge- and spin-density instabilities, a big variety of possible metallic states with spontaneously broken symmetry are found. These states lead to different charge, orbital, spin, and angular momentum ordering patterns. The strong superstructure formation at x = 0.5 is also discussed within this model.

I-R-6 Magnetism in Strongly Correlated and Frustrated Systems

UEDA, Kazuo[1]; YAMASHITA, Yasufumi
([1]Univ. Tokyo)

[*Physica B* **359**, 626–632 (2005)]

In strongly correlated systems, some of the low-energy excitations are enhanced. In geometrically frustrated systems, due to the absence of long-range order, there remains (pseudo-) degeneracy associated with the low-energy excitations at low temperatures. Lifting of degeneracy in both Mott insulating systems and itinerant electron systems are discussed by considering the pyrochlore lattice as an example.

I-S Theory and Applications of Relativistic Quantum-Chemical Methods to Molecular Properties of Compounds Containing Heavy Elements

In our project, we have been developing accurate quantum-chemical theories and methods, we applied these methods to calculations of circular dichroism (CD), magnetic circular dichroism (MCD), and nuclear magnetic resonance (NMR) spectra, in which magnetic interaction and/or electron-spin density play an important role, especially in compounds containing heavy elements. Our progresses in this period are followings. (i) Excitation and CD spectra of dichalcogenide were calculated by the SAC-CI method and the trends of the observed CD spectra were reproduced, and then the mechanism of the well-known C_2 rule and the quadrant rule in C_2 molecules were clarified. (ii) MCD spectra of halogen molecules were calculated by the 2nd-order Douglas-Kroll relativistic method, and some relativistic effects in MCD were discussed. (iii) ^{13}C NMR chemical shifts of CO in various metal complexes interacting with CO, which are models of metal enzymes in biological systems, were calculated and we found that the trend of ^{13}C chemical shifts of CO interacting with various metals were classified by the electron configurations of metals.

I-S-1 Theoretical Studies on Circular Dichroism Spectra of Linear and Cyclic Dichalcogenide Compouns (Chalcogen = S, Se, Te) by the SAC and SAC-CI Methods

SEINO, Junji[1]; HONDA, Yasushi[1]; HADA, Masahiko[2]; NAKATSUJI, Hiroshi[3]
([1]Tokyo Metropolitan Univ.; [2]IMS and Tokyo Metropolitan Univ.; [3]Kyoto Univ.)

[*J. Phys. Chem.* submitted]

We developed a method and a computer software to calculate circular dichroism (CD) intensity in a framework of the SAC/SAC-CI theory. Four chalcogen (Ch) compounds; dihydrogen dichalcogenide, dimethyl dichalcogenide, (+)-bis(2-methylbutyl) dichalcogenide, and 2,3-(R,R) dichalcogenadecalin (chalcogen = S, Se, Te) were treated. As shown in Figure 1, the calculated excitation spectra were in good agreement with the experimental ones, and the calculated CD intensities also reproduce the observed spectra in the low-energy region. In four compounds investigated here, the first and the second bands are assigned to the n-σ^* excitations between the Ch atoms, and the third and the fourth bands are assigned to the n-σ^* excitations between the chalcogen and carbon atoms, respectively. The change in the spectra against the R–Ch–Ch–R dihedral angle revealed the relation between the CD spectra and molecular structures of the dichalcogen compounds. These results were in accordance with the well-know experimental rules, namely the C_2 rule and the quadrant rule. On the other hand, as the chalcogen is heavier, the lowest two bands were calculated to be in the low-energy region. This also agrees with the experimental trends.

The solvent and relativistic effects were not considered in this study, although they are expected to be important in fact. In particular, the treatment of the singlet-triplet coupling will be essential for ditellurides. These are interesting subjects for the study in the near future.

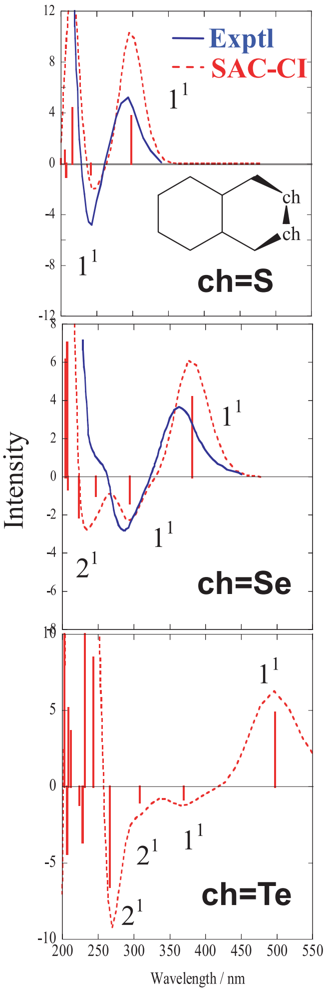

Figure 1. Calculated and observed circular dichroism (CD) spectra of 2,3-(R,R) dichalcogenadecalin (chalcogen = S, Se, Te). The observed spectra are shown by real lines and the calculated ones are shown by dotted lines.

I-S-2 Theoretical Studies on Magnetic Circular Dichroism by the Finite Perturbation Method with Relativistic Corrections

HONDA, Yasushi[1]; HADA, Masahiko[2]; EHARA, Masahiro[3]; NAKATSUJI, Hiroshi[3]; MICHL, J.[4]
([1]Tokyo Metropolitan Univ.; [2]IMS and Tokyo Metropolitan Univ.; [3]Kyoto Univ.; [4]Colorado Univ.)

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

A theoretical method for calculating magnetic circular dichroism (MCD) of molecules was presented. We examined the numerical accuracy and the stability of the finite perturbation (FP) method and the sum-over-state (SOS) perturbation method. The relativistic effects were shown to be important for the MCD spectra of molecules containing heavy elements. Calculations using the FP and the SOS methods were carried out for ethylene, *para*- and *ortho*-benzoquinone (BQ), showing that the FP method was superior to the SOS method, as expected. The differences were not negligible, and even the signs of the terms obtained by the two methods were opposite for the lowest π-π^* states of ethylene. The relativistic effect was examined using the second-order Douglas-Kroll Hamiltonians for the three n-π^* states ($^3\Pi_{1u}$, $^3\Pi_{0u}$, and $^1\Pi_u$) of each of the halogen molecules I_2, Br_2, Cl_2, and F_2. The relativistic effects became important for the MCD spectra of heavy molecules: the Faraday terms of I_2 and Br_2 were strongly affected by the relativistic effects, while the effect was negligible for Cl_2 and F_2. The spin-free relativistic Hamiltonian incorporating the one-electron spin-orbit term gave the results similar to the full relativistic case, indicating that the relativistic effects induced by the two-electron spin-orbit term in MCD are small. In all calculations, the signs of the Faraday terms agreed with those of the experimental values, although some of their absolute values were overestimated compared to the experiments. This was thought to be mainly due to a lack of electron correlation. A two-component quasi-relativistic theory based on the Douglas-Kroll-Hess transformation is developed in order to study a magnetic shielding constant. The Hamiltonian that is proposed in this study is considering the relativistic effect on magnetic vector potential with the Douglas-Kroll theory. The present Hamiltonian can be applied to calculation of magnetic shielding constants, without further expansion in powers of c^{-1}. The calculated results indicated that the relativistic corrections are essential to the theoretical treatments of MCD for molecules containing heavy atoms.

I-S-3 ^{13}C NMR Chemical Shifts of Small Molecules Interacting with Metal Complexes in Heme Proteins and Metal Enzymes

HADA, Masahiko[1]; KUZUOKA, Chie[2]
([1]IMS and Tokyo Metropolitan Univ.; [2]Tokyo Metropolitan Univ.)

[*J. Comput. Chem., Jpn.* to be submitted]

We treated (a) the paramagnetic ^{13}C NMR chemical shifts of CN anion interacting with model complexes of ferric heme proteins and (b) diamagnetic ^{13}C NMR of CO interacting with various imidazole-metal complexes which act as a model of metal enzymes in various biological systems.

(a) The observed paramagnetic carbon-13 chemical shifts of cyanide in ferric porphyrin complexes were recently reported by Fujii. When the trans ligand is a cyanide anion, the shift is –2500 ppm from TMS. When replaced with an imidazole ligand, the shift becomes –4000 ppm. We can observe these chemical shifts over a very wide range. This wide variation of chemical shifts is essentially due to the spin density of the resonance carbon in these open-shell paramagnetic molecules. Therefore, we can use these cyanide-carbon NMR chemical shifts as a probe for testing various heme-protein environments. The trends of ^{13}C chemical shifts in these systems should be clarified by the theoretical methods. The objectives of this theme are followings. (i) Using an accurate quantum-chemical method, SAC/SAC-CI, we present accurate energy-levels for ferric $(d_{xy})^2(d_{xz,yz})^3$ and $(d_{xy})^1(d_{xz,yz})^4$ in bis (cyanide)porphyrinato Iron(III) [FeP(CN)$_2$], bis (cyanide)(*meso*-tetraethyl) porphyrinato Iron(III) [FeTEP(CN)$_2$], and (cyanide) (imidazole) porphyrinato-Iron(III) [FeP(CN-Im)]. (ii) We calculate the paramagnetic ^{13}C NMR chemical shifts of iron-bound ^{13}CN of the above three complexes, both in the ground and low-lying excited states including the ferric $(d_{xy})^2(d_{xz,yz})^3$ and $(d_{xy})^1(d_{xz,yz})^4$ configurations. Then we show the relations between the calculated ^{13}C chemical shifts, the electronic configurations, and the ruffling of the porphyrin rings.

First, we analyzed the ^{13}C chemical shifts of CO in some typical excited states. The temperature dependent Fermi contact term plays an important role to control the ^{13}C chemical shifts of CO by transferring the electron-spin density from the d-orbital of Fe to the CN ligand. This mechanism depends on the electronic configurations of Fe, and is affected sensitively by the trans-ligands.

Second, the effect of deviation of porphyrin ring. The D_{4h} structure becomes the S4 structure by replacing hydrogen atoms with methyl or ethyl groups. The electronic ground state is the B_2 state, though it is the E_g state in the D_4 structure. We found that the ruffling of porphyrin ring drastically affect the chemical shifts of Fe-bounded CN. The total trend of the NMR shifts is controlled by both changing electronic states and ruffling of porphyrin ring.

(b) Various metal-imidazole complexes in metal enzymes interact with CO, were investigated by observing the NMR chemical shifts of ^{13}C of CO. $MIm_3(CO)_2$ ($M = Cr^{2+}$, Fe^{2+}, Cu^+, Zn^{2+}; Im = Imidazole) were used as a model of metal-enzymes. The calculated NMR chemical shifts agree well with the downfield shift observed experimentally in Cu^+. The trend of the ^{13}C NMR chemical shifts were explained by the d-d transition mechanism, namely by the 2nd-order perturbation theory for the paramagnetic term.

I-T Polyamorphism in Molecular Liquids

So far the only quantity known as the order parameter that distinguishes liquids from gases is density. However, a recent experimental confirmation of the very existence of the pressure-induced “structural” transition between stable liquids of black phosphorus lends strong impetus to reconsideration on the concepts of liquids. As represented by amorphous ice, such polyamorphism in metastable states has been known for a long time. Very recently we found that the melting curve of the low-pressure crystalline phase of a molecular crystal $\mathrm{SnI_4}$, which is known to undergo pressure-induced solid-state amorphization, has a maximum at around 2 GPa. This means that an abrupt change in liquid density takes place at that pressure, which is expected to be attributable to liquid-liquid phase transition. The purpose of the project is not only to experimentally reveal the transition but also to construct the statistical-mechanical model for the transition from which order parameters other than the density characterizing the polyamorphism can be extracted.

I-T-1 Construction of an Interaction-Site Model for Molecular Systems

FUCHIZAKI, Kazuhiro
(IMS and Ehime Univ.)

Our target substance is a molecular crystal $\mathrm{SnI_4}$, which exhibits a variety of structural and electrical properties under high pressures.[1] Although our model crystalline with octupole-octupole interactions entered as the first nonvanishing contribution to the perturbed part exhibited considerably higher melting points[2] compared to the experimental results,[3] investigations on the liquid state utilizing this model is still attractive, since no experimental information under high pressures has been as yet available. However, actual numerical computations are much time-consuming. Hence, to set up a new interactions-site model that can deal with molecular systems more efficiently in the simulations is by no means trivial.

Let us suppose molecular systems consisting of electrically neutral molecules with internal degrees of freedom. We assume that the intermolecular interactions are given by the sum of the interactions between the interaction sites within a molecule. The constituent interaction is proportional to the inverse power s of a distance between the interaction sites. Let $\mathbf{r}_i$ be the center-of-mass position of the ith molecule. The position of the kth interaction site relative to $\mathbf{r}_i$ is given by $\alpha^k\mathbf{p}_i^k$, $\mathbf{p}_i^k$ being fixed to the molecule. We locate a “charge” at the interactions site, which is denoted by $\zeta_i^k(s)$. The quotation marks are intended to mean that the charges are ordinary electric charges when $s = 1$, but otherwise, they are virtual whose magnitude yields the units of [energy][(length)^s] when multiplied with each other. This generalization of the concept of charges allows us to treat the interaction sites in a unified fashion without regarding the Coulombic interaction sites as being special. We then arrange these molecules in a p-dimensional computational cell, whose basis vectors are given by $[\mathbf{u}_1, \mathbf{u}_2, \ldots, \mathbf{u}_p] = \mathbf{h}$. When the periodic boundary condition is imposed, the position of kth interaction site within ith molecule in mth image cell is given by $\mathbf{r}_m + \mathbf{r}_i + \alpha^k\mathbf{p}_i^k = \mathbf{r}_m + \mathbf{r}_i^k(\alpha^k)$. Here, $\mathbf{r}_m = \mathbf{hm}$, $\mathbf{m}$ being the vector whose components are all integers. Then, total intermolecular interaction is given by $\Phi = \Sigma_s\Phi(s;p)$ with

$$\Phi(s;p) = \frac{1}{2}\sum_{m}\sum_{i}\sum_{k\in i}\sum_{j}\sum_{l\in j}\frac{\varsigma_i^k(s)\varsigma_j^l(s)}{\left|\mathbf{r}_m + \mathbf{r}_{ij}^{kl}(\alpha^k(s);\alpha^l(s))\right|^s},$$

where $\mathbf{r}_{ij}^{kl}(\alpha^k(s);\alpha^l(s)) = \mathbf{r}_i^k(\alpha^k) - \mathbf{r}_j^l(\alpha^l)$. The lattice sums appearing in this expression corresponds to a special case of the generalized zeta function of pth order developed by the author.[4] Derivation of the final expression for $\Phi(s;p)$ together with some examples of its implementation will soon be reported.

References

1) N. Hamaya, K. Sato, K. Usui-Watanabe, K. Fuchizaki, Y. Fujii and Y. Ohishi, *Phys. Rev. Lett.* **79**, 4597–4600 (1997).
2) K. Fuchizaki and K. Nagai, *Solid State Commun.* **132**, 305–308 (2004).
3) K. Fuchizaki, Y. Fujii, Y. Ohishi, A. Ohmura, N. Hamaya, Y. Katayama and T. Okada, *J. Chem. Phys.* **120**, 11196–11199 (2004).
4) K. Fuchizaki, *J. Phys. Soc. Jpn.* **63**, 4051–4059 (1994).

I-U Nonlinear Processes Induced by Ultrafast Laser Pulses

Recent technological progress on the generation of intense XUV pulses has opened up a new field on ultrafast and nonlinear optics. Commercial femtosecond Ti:Sapphire laser systems typically produce light pulses with pulse durations of tens of fs around the wavelength of 800 nm. Recalling that the optical cycle of the 800 nm light pulse is 2.7 fs, the pulse duration of tens of fs implies that tens of cycles are contained in a single pulse. When the number of the cycles decreases down to a few-cycle, new phenomena which are dependent on the carrier-envelope phase (absolute phase) emerge. In this project, we have carried out theoretical investigation related to the few-cycle pulse.

I-U-1 Few-Cycle Effects in the Low Intensity Regime

NAKAJIMA, Takashi[1]; WATANABE, Shuntaro[2]
([1]IMS and Kyoto Univ.; [2]Univ. Tokyo)

One of the most fascinating features induced by few-cycle-pulses is that laser-induced dynamics such as ionization and high harmonic generation have a dependence on the carrier-envelope-phase (CEP). Naturally any kinds of CEP effects will be easily smeared out if the CEP is not stabilized on the shot-to-shot basis. Whether and how much CEP effects we can see depends on the number of cycles and pulse intensity, and the dependence is different for different systems even with the same pulse conditions. In the intensity region where tunneling ionization plays a major role, the dynamics can be rather well described using a semi-classical theory, *i.e.*, quasi-static tunneling theory for ionization, with the help of classical mechanics after the electron ejection, and it was shown that photoelectron yields exhibit a clear CEP dependence. In the weaker intensity region, however, tunneling ionization hardly takes place and multiphoton ionization is the dominant process for ionization. It has not yet been clarified whether and how much CEP effects can be seen in the weaker intensity region. We have theoretically studied the CEP effects in this intensity regime and found significant CEP effects in terms of the total ionization yield and the bound state population of atomic systems.

I-V Control of Photoionization Processes Using Lasers

Optical control of various photoexcitation processes are of great interest in recent years, which is termed "coherent control." In this project, we have theoretically explored the possibility to control spin-polarization and the ejection angle of photoelectrons.

I-V-1 Control of the Spin-Polarization of Photoelectrons/Photoions Using Short Laser Pulses

NAKAJIMA, Takashi
(IMS and Kyoto Univ.)

[*Appl. Phys. Lett.* **84**, 3786–3788 (2004)]

Since highly spin-polarized species such as electrons, ions, and nucleus, *etc.*, are very useful in various fields, developing a new method to control the spin degree of freedom is one of the most important issues in modern technology and science. Recently we have theoretically proposed a generic pump-probe scheme to control spin-polarization of photoelectrons/photoions by short laser pulses. The validity of the theoretical treatment, however, has been limited to the weak field in which a very small fraction of atoms are pumped to the excited states. For the maximum production of spin-polarized ions/electrons, it is desired to use strong pump/probe pulses. Based on the Schrödinger equation, we have developed a theory of spin-polarization so that the laser intensities can be arbitrarily strong. By numerically solving the derived equations for the realistic scheme of Mg atom, we have found a intensity-dependent spin-polarization.

I-V-2 Control of Photoelectron Angular Distributions Using a Dressing Laser

NAKAJIMA, Takashi[1]; BUICA, Gabriela[2]
([1]IMS and Kyoto Univ.; [2]Kyoto Univ.)

[*Phys. Rev. A* **71**, 013413 (2005)]
[*Phys. Rev. A* **72**, 053416 (2005)]

Strong dressing laser field can induce various interesting modification in laser-matter interactions. Among them, an interesting modification is observed in the photoionization spectra in the wavelength region at which two-photon near-resonance is satisfied for the initially occupied state by a probe laser and initially unoccupied state by a dressing laser. This is known as laser-induced continuum structure (LICS). Recently we have reported the theoretical analysis of LICS for the K atom in terms of the modification of photoelectron angular distribution, where the geometry of laser polarization has been limited to the case in which both probe and dressing lasers are linearly polarized and parallel.

We have obtained strong modifications, as a function of the two-photon laser detuning and the dressing laser intensity, in the photoelectron distribution and the branching ratios into different ionization continua.

We have further extended the analysis for the case with a variable polarization angle. Again, a significant polarization-angle dependence has been found in terms of the photoelectron angular distribution and the branching ratios into the different ionization continua.

I-W Theoretical Studies on Dynamical Foundation of Chemical Reactions and Proteins

Recent experimental developments in single molecule spectroscopy have shed light on the distinct nonergodic features and the heterogeneity of the state space and non-Markovian process of biomolecules. This project focuses on the dynamical foundation of chemical reactions, *i.e.*, why and how do the reacting systems climb through the saddle? and on the developments of new time series analyses to extract the dynamical information regarding the underlying state space structure from single molecule time series.

I-W-1 Phase Space Reaction Network on Multibasin Energy Landscapes

LI, Chun Biu[1,2]; MATSUNAGA, Yasuhiro[1]; TODA, Mikito[3]; KOMATSUZAKI, Tamiki[1,2,4]
([1]Kobe Univ.; [2]JST/CREST; [3]Nara Women's Univ.; [4]IMS)

[*J. Chem. Phys.* **123**, 184301 (13 pages) (2005)]

Recent theoretical developments[1–4)] in chemical reactions have greatly improved our understanding of the definability of the no-return dividing hypersurface and the reaction path along which all reacting species follow. By using the HCN/CNH isomerization reaction as an illustrative vehicle of chemical reactions on multibasin energy landscapes, we give explicit visualizations of molecular motions associated with straight-through reaction tube in the phase space inside which all reactive trajectories pass from one basin to another, with eliminating recrossing trajectories in the configuration space. This visualization provides us with a chemical intuition of how chemical species "walk along" the reaction rate slope in the multi-dimensional phase space compared with the intrinsic reaction path in the configuration space. The distinct nonergodic features in the two different HCN and CNH wells can be easily demonstrated by a section of Poincaré surface of section in those potential minima, which predicts *a priori* the pattern of trajectories residing in the potential well. We elucidate the global phase space structure which gives rise to non-Markovian dynamics or dynamical correlation of sequential multi-basin chemical reactions. The controllability of the product state in chemical reactions is also presented in terms of the phase space structure.

References

1) T. Komatsuzaki and R. S. Berry, *Proc. Natl. Acad. Sci. U.S.A.* **98**, 7666 (2001).
2) T. Komatsuzaki and R. S. Berry, *J. Chem. Phys.* **130**, 4105 (2001).
3) T. Komatsuzaki and R. S. Berry, *Adv. Chem. Phys.* **123**, 79 (2002).
4) M. Toda, T. Komatsuzaki, T. Konishi, R. S. Berry and S. A. Rice, Eds., "Geometrical Structures of Phase Space in Multidimensional Chaos: Applications to Chemical Reaction Dynamics in Complex Systems," *Adv. Chem. Phys.* **130A,130B** (2005).

I-W-2 A Construction of Multidimensional Free Energy Landscape from an Ensemble of Single Molecule Time Series

BABA, Akinori[1,2]; KOMATSUZAKI, Tamiki[1,2,3]
([1]Kobe Univ.; [2]JST/CREST; [3]IMS)

Recent experimental developments in single molecule spectroscopy hold great promise to shed light on the complexity of dynamics of biomolecules. However, without any knowledge about the potential energy function and the number of energy basins with the metric relation among them, what can we learn from an observed single molecule scalar time series about the multivariate free energy landscape or, in general, state space structure buried in the observations?

Using local ergodicity ansatz as a 0th order description, we developed a new empirical self-consistent scheme to elucidate the local ergodic state distribution function from an ensemble of short single molecule time series and construct an effective multidimensional free energy landscape where local ergodic states are located with preserving the "metric" relationship among them as possible in the projected space. We also proposed the transition sequence analysis to elucidate the degree of memory along each transition sequence path.

I-W-3 A New Technique to Differentiate the Origin of Observed non-Brownian Dynamics in the Principal Component Space

MATSUNAGA, Yasuhiro[1]; LI, Chun Biu[1,2]; KOMATSUZAKI, Tamiki[1,2,3]
([1]Kobe Univ.; [2]JST/CREST; [3]IMS)

The dimensional reduction is crucial to focus on some important degrees of freedom in manybody protein dynamics. The principal component (PC) analysis is one of the most widely used methods and the projection of protein dynamics on the PC space have often shown large deviations from a simple normal Brownian picture, for example, in Crambin in crystal,[1)] Cytochrome *c* in water,[2)] Plastocyanin in water.[3)] However, it was derived analytically[4)] that multidimensional normal Brownian motion can also exhibit the regular behavior on the PC space deviated from normal Brownian motion. What can we learn from the projection of complex protein dynamics onto the PC space?

We developed a new diagnostic technique to differentiate the origin of the observed regular behavior in order to extract essential (rather than artifact) information inherent to the dynamics of the protein by using finite size Liapunov exponent concept5),6) and the PC eigenvalue spectrum.7)

References

1) A. E. García, R. Blumenfeld, G. Hummer and J. A. Krumhansl, *Physica D* **107**, 225 (1997).
2) A. E. García and G. Hummer, *Proteins* **36**, 175 (1999).
3) P. Carlini, A. R. Bizzarri and S. Cannistraro, *Physica D* **165**, 242 (2002).
4) B. Hess, *J. Chem. Phys.* **62**, 8438 (1999).
5) G. Paladin, M. Serva and A. Vulpiani, *Phys. Rev. Lett.* **74**, 66 (1995).
6) T. Shibata and K. Kaneko, *Physica D* **124**, 177(1998).
7) J. B. Gao, Y. Cao and J. -M. Lee, *Phys. Lett. A* **314**, 392 (2003).

I-W-4 Polypeptide in Water on the Lagrange Picture in Fluid Dynamics

NODA, Satoshi[1]; BABA, Akinori[1,2]; KOMATSUZAKI, Tamiki[1,2,3]
([1]Kobe Univ.; [2]JST/CREST; [3]IMS)

The (overdamped) Langevin formulation has been one of the most utilized methods in describing complex dynamics of biomolecules in solution. This is based on an implicit assumption of the existence of separable time scales between the global dynamics of biomolecules and those of the surrounding solvents. However, recently, it was revealed for human Lysozyme in solution1),2) that the rotational diffusion of *local dipole field*, which is defined as a short time ensemble average of the dipole moment vectors of many individual water molecules at a solvent site through which they pass or visit, has dynamical memory up to 70 times longer than the rotational relaxation of the individual water molecules in the vicinity of human Lysozyme. This indicates that the time separability required for validating the Langevin formulation does not necessarily hold and water molecules may not necessarily retard the protein motions as “friction.” We examined a dynamic inseparability of helix-coil transition of polyalanine and the surrounding water rearrangement by investigating the correlation between individual site dipole vector field and turn moiety dynamics of polyalanine. We found that, at the turn formation, the site-dipole field dynamics and turn formation is correlated more significant than those before and after the formation, that is consistent with the computational mechanics analysis for Leu-Enkephalin in solution.3)

References

1) J. Higo, *et al., Proc. Natl. Acad. Sci. U.S.A.* **98**, 5961 (2001).
2) T. Yokomizo, S. Yagihara and J. Higo, *Chem. Phys. Lett.* **374**, 453 (2003).
3) D. Nerukh, G. Karvounis and R. C. Glen, *Complexity* **10**, 40 (2004).