

RESEARCH ACTIVITIES I

Department of Theoretical Studies

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

It is an important subject to develop molecules with novel bonding and structures. Thus, multiple bonds between heavier atoms are investigated which are the focus of interest as new building block for molecular design. In addition, large cage-like molecules and clusters are investigated to characterize guest-host interactions, which serve as molecular containers and recognition. To develop new reactions, the catalytic reactions of enzymes are investigated. A theoretical method to predict molecular crystal structures is in progress.

I-A-1 A Silicon-Silicon Triple Bond Surrounded by Bulky Terphenyl Groups

TAKAGI, Nozomi; NAGASE, Shigeru

[*Chem. Lett.* 966 (2001)]

Since the first synthesis in 1981, a number of stable silicon-silicon doubly bonded compounds have been synthesized and isolated. However, stable silicon-silicon triply bonded compounds, disilynes ($RSi\equiv SiR$), are still unknown, which are the focus of interest in silicon chemistry. In search of an isolable disilyne, effects of bulky terphenyl groups on silicon-silicon triple bonding are investigated. It is predicted that $Ar^*Si\equiv SiAr^*$ ($Ar^* = 2,6$ -bis(2,4,6-triisopropylphenyl)phenyl) is an interesting synthetic target.

I-A-2 The Quest of Stable Silanones: Substituent Effects

KIMURA, Masahiro; NAGASE, Shigeru

[*Chem. Lett.* 1098 (2001)]

Recent remarkable progress in the heavier analogues of ketones is marked by the isolation of silanethione ($R_2Si=S$) and silaneselone ($R_2Si=Se$). As the member of this family, however, isolable silanones ($R_2Si=O$) are still missing except for the transient intermediates and spectroscopic detection, because of the high reactivities due to the polarized $Si^{\delta+}=O^{\delta-}$ bond. DFT and ONIOM calculations are systematically carried out to suppress the high reactivities. Several isolable silanones are predicted, which are worthy of experimental testing.

I-A-3 Substituent Effects on Germanium-Germanium and Tin-Tin Triple Bonds

TAKAGI, Nozomi; NAGASE, Shigeru

[*Organometallics* 20, 5498 (2001)]

Triple bonds between heavier main group elements are of widespread interest. We have suggested that disilynes ($RSi\equiv SiR$) are a viable synthetic target when they bear proper bulky substituents [*Organometallics*

20, 234 (2001)]. It is an important question whether the still heavier analogues are also synthetically accessible and isolable as stable molecules. Effects of bulky aryl groups such as $C_6H_2-2,4,6-\{CH(SiMe_3)_2\}_3$ and $C_6H_3-2,6-(C_6H_2-2,4,6-i-Pr_3)_2$ on germanium-germanium and tin-tin triple bonds are theoretically investigated in search of isolable digermynes ($RGe\equiv GeR$) and distannynes ($RSn\equiv SnR$).

I-A-4 Theoretical Study of an Isolable Compound with a Short Silicon-Silicon Triple Bond; $(tBu_3Si)_2MeSiSi\equiv SiSiMe(Si^tBu_3)_2$

TAKAGI, Nozomi; NAGASE, Shigeru

[*Eur. J. Inorg. Chem.* 2775 (2002)]

According to our theoretical investigations [*J. Organomet. Chem.* 611, 264 (2000)], electropositive silyl groups are electronically more effective than aryl groups in realizing a less trans-bent disilyne with a short silicon-silicon triple bond. However, it has been found that silyl groups such as Si^tBu_3 and $SiDep_3$ ($Dep = 2,6$ -diethylphenyl) are not sufficiently bulky to make disilynes isolable under normal conditions. Therefore, the effects of a very bulky silyl group, $R^{**} = SiMe(Si^tBu_3)_2$, on silicon-silicon triple bonding are investigated using density functional theory. It is found that $R^{**}Si\equiv SiR^{**}$ is stable enough to be isolable and has a silicon-silicon triple bond that is as short as 2.072 Å.

I-A-5 Interesting Compounds Featuring Double Bonding between Heavier Group 15 Elements

SASAMORI, Takahiro¹; TAKEDA, Nobuhiro¹; TOKITOH, Norihiro¹; OKAZAKI, Renji³; KIMURA, Masahiro; NAGASE, Shigeru
(¹Kyoto Univ.; ²Japan Women's Univ.)

[*Angew. Chem. Int. Ed.* 41, 139 (2002)]

[*Bull. Chem. Soc. Jpn.* 75, 661 (2002)]

Distibene ($RSb=SbR$), dibismuthene ($RBi=BiR$), and phosphabismutene ($RP=BiR$) have been synthesized by taking advantage of steric protection using an efficient steric protection group, $C_6H_2-2,4,6-\{CH(SiMe_3)_2\}_3$, as the first examples of double bonds to fifth-row and six-

row elements in group 15. The structural features are investigated using density functional theory by changing the substituent groups.

I-A-6 The First Halogen-Substituted Cyclotrimerenes: A Unique Halogen Walk over the Three-Membered Skeleton and Facial Stereoselectivity in the Diels-Alder Reaction

SEKIGUCHI, Akira¹; ISHIDA, Yutaka¹; FUKAYA, Norihisa¹; ICHINOHE, Masaki¹; TAKAGI, Nozomi; NAGASE, Shigeru
(¹Univ. Tsukuba)

[*J. Am. Chem. Soc.* **124**, 1158 (2002)]

Unsaturated three-membered ring compounds consisting of heavier group 14 elements, cyclotrimetallenes, have attracted considerable attention because of their unique structures; the chemistry has developed very rapidly. However, the heteroatom-substituted cyclotrimetallenes are unknown because of the synthetic difficulty and instability. By introducing electronegative halogen atoms, the first hetero-substituted cyclotrimerenes are synthesized and the structural features are theoretically investigated. The interaction between the low-lying σ^* (Ge-halogen) and high-lying endocyclic π (Ge=Ge) orbitals play an important role.

I-A-7 Effects of the σ^* Orbital of C-Apical O-Equatorial Spirophosphoranes on the Structure, Stereomutation, and Reactivity

AKIBA, Kin-ya¹; MATSUKAWA, Shiro²; ADACHI, Takahiro²; YAMAMOTO, Yohsuke²; RE, Suyong; NAGASE, Shigeru
(¹Waseda Univ.; ²Hiroshima Univ.)

[*Phosphorus, Sulfur Silicon Relat. Elem.* **177**, 1671 (2002)]

[*J. Am. Chem. Soc.* **124**, 13154 (2002)]

Interesting effects of the σ^* orbital of C-apical O-equatorial (O-*cis*) spirophosphoranes are investigated from theoretical and experimental points of view. It is experimentally found that O-*cis* phosphoranes are much more electrophilic on the phosphorus atom than the O-*trans* isomers. It is calculated that the $\sigma^*_{\text{P-O}}$ orbital level of O-*cis* phosphoranes is 19 kcal/mol lower than the $\sigma^*_{\text{P-C}}$ orbital level of O-*trans* phosphoranes. The low-lying σ^* orbital plays an important role in enhancing the electrophilicity of spirophosphoranes.

I-A-8 Theoretical Calculations of Vibrational Modes in Endohedral Metallofullerenes: La@C₈₂ and Sc₂@C₈₄

KOBAYASHI, Kaoru; NAGASE, Shigeru

[*Mol. Phys.* in press]

The electronic properties and reactivities of endohedral metallofullerenes have been extensively investigated both theoretically and experimentally. The metal

motion and cage structure are currently of considerable interest in the far-infrared and Raman spectroscopic study. Thus, theoretical calculations are performed for the representative metallofullerenes, La@C₈₂ and Sc₂@C₈₄, to provide insight into the metal-cage vibrational modes as well as cage structures. The La-based vibrational modes and wave numbers calculated for La@C₈₂ are in good agreement with those assigned experimentally. An interesting finding is that the vibrational frequencies are little changed upon reduction or oxidation. The Sc-based vibrations calculated for Sc₂@C₈₄ are also compared with the available experimental data. In addition, the structures of the Sc₂@C₈₄ isomers are discussed.

I-A-9 A Stable Unconventional Structure of Sc₂@C₆₆ Found by Density Functional Calculations

KOBAYASHI, Kaoru; NAGASE, Shigeru

[*Chem. Phys. Lett.* **362**, 373 (2002)]

In 1997 we predicted that the isolated pentagon rule (IPR) established in fullerene chemistry could be violated by metal-mediated interactions [*J. Am. Chem. Soc.* **119**, 12693 (1997)]. In this context, the recent isolation of Sc₂@C₆₆ and Sc₃N@C₆₈ is noteworthy because there is no IPR-satisfying isomer between C₆₀ and C₇₀. The cage structure and metal position of Sc₂@C₆₆ are theoretically determined. Interestingly, the endohedral C_{2v} structure determined by MEM/Rietveld analysis of the X-ray powder data [*Nature* **408**, 426 (2000)] does not correspond to an energy minimum but collapses with no barrier. Instead, a much more stable C_{2v} structure with two pairs of three-fold fused pentagons is found, which satisfies the observed ¹³C NMR spectrum. Two Sc atoms are highly stabilized in the non-classical C₆₆ cage by electrostatic interactions induced by electron transfer from Sc to C₆₆.

I-A-10 Theoretical Study of the Cations and Anions of La₂@C₈₀ and Sc₃N@C₈₀

MAYER, Bodo¹; KOBAYASHI, Kaoru; NAGASE, Shigeru
(¹IMS and TU-Darmstadt)

Theoretical calculations are performed for the neutral, anionic, and cationic states of La₂@C₈₀ and Sc₃N@C₈₀. It is found that added electrons are localized on the encapsulated metal atoms while electron removal takes place from the carbon cage. As the number of added electrons increases, the spherical carbon cage transforms to an ellipsoid structure and the metal positions is changed. The electron density difference maps reveal the important changes in electronic structures upon reduction and oxidation.

I-A-11 Theoretical Identification of the Structures of C₂₀: Prevalence of the Monocyclic Isomer and Existences of the Smallest Fullerene and Bowl Isomers

LU, Jing¹; RE, Suyong; CHOE, Yoong-Kee; NAGASE, Shigeru; ZHOU, Yunsong²; HAN, Rushan²; PENG, Lianmao²; ZHANG, Xinwei²; ZHAO, Xiangeng²
(¹IMS and Peking Univ.; ²Peking Univ.)

[*Phys. Rev. B* submitted]

Free energies, electron affinities and vibrational modes of C₂₀ isomers are theoretically investigated. The major C₂₀ isomer generated by vaporizing graphite has a monocyclic ring, followed by a tadpole (a short chain attached to a monocyclic ring), chain, and a bicyclic ring. On the other hand, the two C₂₀ isomers synthesized recently [*Nature* **407**, 60 (2000)] have fullerene and bowl structures.

I-A-12 The Size of Silicon Clusters Suitable for Endohedral Metal-Doping

LU, Jing¹; NAGASE, Shigeru
(¹IMS and Peking Univ.)

Structures and electronic properties of metal-doped silicon clusters MSi_n (M = W, Zr, Os, Pt, and Co; n = 8–20) are theoretically investigated. In contrast to a recent experiment [*Phys. Rev. Lett.* **86**, 1733 (2001)] suggesting that a metal atom is encapsulated inside the Si_n cluster, formation of endohedral structures depends strongly on the size of silicon clusters. In addition, several novel stable endohedral structures are found. The size of stable endohedral forms is predicted to be in the range 10 ≤ n ≤ 16.

I-A-13 What is the Smallest Metal-Encapsulated Germanium Clusters?

LU, Jing¹; NAGASE, Shigeru
(¹IMS and Peking Univ.)

Metal-doped germanium clusters MGe_n (M = Hf, W, Os, Ni, and Zn) are investigated using density functional calculations. The smallest metal-encapsulated germanium cluster contain 13 germanium atoms and takes a distorted hexagonal prism structure (W@Ge₁₂ and Os@Ge₁₂). These size and shape differ from those of the smallest metal-encapsulated silicon cluster that contains 11 silicon atoms and has a basketlike structure. The stable ZnGe₁₂ structure is exohedral, although an endohedral icosahedral structure is suggested in a recent theoretical study [*Appl. Phys. Lett.* **80**, 859 (2002)].

I-A-14 Host-Guest Interaction in Molecular Capsule Formation

RE, Suyong; NAGASE, Shigeru

It is of current synthetic interest to develop functional molecular capsules. Carceplex is a complex in which guest molecules are entrapped by a container host molecule. Although it is known that guest molecules act as a template, the encapsulation mechanism is not fully understood. Small changes in the size and shape of guest molecules lead to remarkable changes in the yield

of carceplex. Since the efficient synthesis of carceplex depends strongly on the type of guest molecules, host-guest interactions are systematically investigated by theoretical calculations to reveal the details of formation mechanism.

I-A-15 Does the Axial Ligand of Iron (IV)-Oxo-Porphyrin Affect the Reactivity of Cytochrome P450?

CHOE, Yoong-Kee; NAGASE, Shigeru

Hemoenzymes play versatile roles in living organisms. However, the origin of their various functions has not been fully understood. Among these, alkane hydroxylation by cytochrome P450 has been a subject of intense studies because the reaction intermediates have not been captured experimentally. It has been considered that the coordination of cysteine to heme is responsible for the catalytic action of cytochrome P450. However, there has been much debate on the role of the axial cysteine ligand. Therefore, density functional calculations have been carried out to investigate the roles of the axial cysteine ligand of the iron (IV)-oxo-porphyrin intermediate (compound I) that is generated in the alkane hydroxylation catalyzed by cytochrome P450. The ligand effects are compared with those in enzymes such as tyrosine and histidine.

I-A-16 A Nonspectroscopic Method to Determine the Photolytic Decomposition Pathways of 3-Chloro-3-Alkyldiazirine; Carbene, Diazo and Rearrangement in Excited State

WAKAHARA, Takatsugu¹; NIINO, Yasuyuki²; KATO, Takashi²; MAEDA, Yutaka¹; AKASAKA, Takeshi¹; LIU, Michael T. H.³; KOBAYASHI, Kaoru; NAGASE, Shigeru
(¹Univ. Tsukuba; ²Niigata Univ.; ³Univ. Prince Edward Island)

[*J. Am. Chem. Soc.* **124**, 9465 (2002)]

The C₆₀ fullerene acts as a mechanistic probe for the formation of carbene, diazo compound, and for the rearranged product via the excited state in the photolysis of 3-chloro-3-isopropyl-diazirine and 3-chloro-3-chloromethyl-diazirine. The carbene adds to C₆₀ to form methanofullerene, whereas the diazo compound adds to C₆₀ to form fulleroid. The olefin product arises as a result of the rearrangement in the excited state

I-A-17 Prediction of Molecular Crystal Structures by an Ab Initio Pair Potential Method

NAGAYOSHI, Kanade¹; KITaura, Kazuo²; NAGASE, Shigeru
(¹IMS and Osaka Prefecture Univ.; ²AIST)

It is an important subject to predict the structures of molecular crystals from the component molecules. Therefore, several methods have been suggested to predict crystal structures using empirical atom-atom

potentials. However, these empirical methods are not sufficiently reliable to be widely applicable. Instead, we developed an efficient method to predict lattice constants using ab initio pair potentials. It is the advantage that lattice constants can be calculated without empirical parameters, even if crystals contain any atoms. To realize high-speed calculations, a parallel computing program is developed on PC clusters.

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

Prediction of the three-dimensional structures of protein molecules by computer simulations is a very challenging problem in theoretical molecular science. The difficulty of the problem lies in two facts: (1) the inclusion of accurate solvent effects is non-trivial and time-consuming (2) there exist 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.

I-B-1 Replica-Exchange Monte Carlo Simulation of a Small Peptide in Aqueous Solution Based on the RISM Theory

mitsutake, Ayori¹; KINOSHITA, Masahiro²; OKAMOTO, Yuko; HIRATA, Fumio
(¹Keio Univ.; ²Kyoto Univ.)

We performed a replica-exchange Monte Carlo simulation of a penta peptide, Met-enkephalin, in aqueous solution that is based on the reference interaction site model (RISM) theory. The RISM theory has been developed from the statistical mechanics of molecular liquids and can calculate the solvation free energy of solute molecules, which depends on temperature. When the total energy depends on temperature, we need to modify the transition probability of replica-exchange process in replica-exchange Monte Carlo simulation. In this paper, we give the formula for the modification of this transition probability and present the results of this simulation.

I-B-2 Comparison of AMBER, CHARMM, OPLS, and GROMOS Force Fields by Generalized-Ensemble Simulations

YODA, Takao; SUGITA, Yuji¹; OKAMOTO, Yuko
(¹Univ. Tokyo)

In order to succeed in the prediction of protein tertiary structures from the first principles, it is essential that we have an accurate potential energy function, or force field, for the protein system. Commonly used force fields are AMBER, CHARMM, OPLS-AA, and GROMOS. In the present work we try to compare these force fields. Our criterion for good force fields is whether or not molecular simulations of short peptide systems in explicit water can reproduce experimental implications of secondary structure formations such as α -helix and β -hairpin, starting from completely random initial conformations. For this purpose it is very important that we use a powerful simulation algorithm that can avoid getting trapped in states of energy local minima. Generalized-ensemble algorithms are such powerful algorithms. In particular, we use our new generalized-ensemble algorithms, replica-exchange multicanonical algorithm and multicanonical replica-exchange method. Indeed we found very different results depending on the force fields; some contradict with the experiments.

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 An Application of the Multicanonical Monte Carlo Method to the Bulk Water System

MUGURUMA, Chizuru¹; OKAMOTO, Yuko; MIKAMI, Masuhiro²
(¹Chukyo Univ.; ²AIST)

[submitted for publication]

The multicanonical algorithm is based on a non-Boltzmann weight factor and produces flat probability distribution of potential energy artificially. The method allows the system to rove through the complex potential

energy surface without getting trapped in a local minimum state, and has been proven to be efficient for studying first-order phase transitions of complex systems such as spin glasses and proteins. One of the features of the method is that the expectation values of thermodynamic properties can be calculated as a function of temperature by applying the histogram-reweighting techniques to the results of one production run. In the present study, we determined the multicanonical weight factor that can produce flat probability distribution of potential energy corresponding to the temperature range from 170 to 630 K. From the peak of the heat capacity, we found a phase transition at 190 K.

The lower energy structures and oxygen-oxygen radial distribution functions imply that the structure at lower temperatures is irregular. However, the average number of hydrogen bonds per water molecule is nearly equal to four at low temperatures, which suggests the formation of amorphous ice.

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

I-D-1 Significant Improvement of the Trajectory Surface Hopping Method by the Zhu-Nakamura Theory

ZHU, Chaoyuan; KAMISAKA, Hideyuki¹;
NAKAMURA, Hiroki
(¹GUAS)

[*J. Chem. Phys.* **115**, 11036 (2001)]

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

I-D-2 New Implementation of the Trajectory Surface Hopping Method with Use of the Zhu-Nakamura Theory. II. Application to the Charge Transfer Processes in the 3D DH_2^+ System

ZHU, Chaoyuan; KAMISAKA, Hideyuki¹;
NAKAMURA, Hiroki
(¹GUAS)

[*J. Chem. Phys.* **116**, 3234 (2002)]

The newly implemented trajectory surface hopping (TSH) method for the collinear system with use of the Zhu-Nakamura semiclassical theory of nonadiabatic transition [C. Zhu, K. Nobusada, and H. Nakamura, *J. Chem. Phys.* **115**, 3031 (2001)] is extended to treat 3D nonadiabatic reactions. Since the avoided crossing seam becomes a two-dimensional surface in the 3D system, the nonadiabatic transition region and the possibility of classically forbidden hops are enlarged very much in

comparison with those in the collinear case. As a result, the contribution of the classically forbidden hops is quite a bit enhanced in the 3D system. Conservation of total angular momentum J is taken into account by slightly rotating the direction of momentum during the hop in the classically forbidden case. The method is tested by applying to the charge transfer processes in the 3D DH_2^+ system for $J = 0$. Numerical results clearly demonstrate that the new TSH method works very well at all energies and for all initial vibrational states considered compared to the old TSH method based on the Landau-Zener formula. The significant discrepancy between the two TSH methods survives even at high collision energy and high vibrational states in contrast to the collinear case, indicating the importance of the classically forbidden hops in 3D systems. The new TSH method is considered to be a very promising method to deal with high dimensional nonadiabatic dynamics. It should also be noted that the new TSH method does not require any knowledge of nonadiabatic coupling and is based only on adiabatic potentials.

I-D-3 Elucidations of Nonadiabatic Tunneling Type and Conical Intersection Type Reactions with Use of the Zhu-Nakamura Theory

ZHU, Chaoyuan; MIL'NIKOV, G. V.¹;
NAKAMURA, Hiroki
(¹IMS and Inst. Struct. Macrokinetics, Russia)

Based on the model 3D potential energy surfaces, electronically nonadiabatic chemical reaction dynamics are investigated with use of the Zhu-Nakamura theory. The trajectory surface hopping method and the IVR type semiclassical propagation method are employed. The dynamics are compared with the exact quantum computations and also with the usage of the Landau-Zener formula. It is aimed to develop a practically useful methodology applicable to multi-dimensional dynamics.

I-E Theory of Nonadiabatic Transitions

I-E-1 Nonadiabatic Transition: Concepts, Basic Theories and Applications

NAKAMURA, Hiroki

[*Nonadiabatic Transition: Concepts, Basic Theories and Applications* World Scientific / Imperial College Press; Singapore (2002)]

- Chapter 1 Introduction: What is "Nonadiabatic Transition" ?
- Chapter 2 Multi-Disciplinarity
- Chapter 3 Historical Survey of Theoretical Studies

- Chapter 4 Background Mathematics
- Chapter 5 Basic Two-State Theory for Time-Independent Processes
- Chapter 6 Basic Two-State Theory for Time-Dependent Processes
- Chapter 7 Two-State Problems
- Chapter 8 Effects of Dissipation and Fluctuation
- Chapter 9 Multi-Channel Problems
- Chapter 10 Multi-Dimensional Problems
- Chapter 11 Complete Reflection and Bound States in the Continuum
- Chapter 12 New Mechanism of Molecular Switching
- Chapter 13 Control of Nonadiabatic Processes by an

External Field

Chapter 14 Conclusions: Future Perspectives

Appendix A Final Recommended Formulas for General Time-Independent Two-Channel Problem

Appendix B Time-Dependent Version of the Zhu-Nakamura Theory

I-E-2 Semiclassical Theory of Nonadiabatic Transition and Tunneling**ZHU, Chaoyuan; MIL'NIKOV, G. V.¹;
NAKAMURA, Hiroki***(¹IMS and Inst. Struct. Macrokinetics, Russia)**[Modern Trends in Chemical Reaction Dynamics K. Liu and X. Yang, Eds., Advanced Series in Physical Chemistry, World Scientific (2003)]*

1. Introduction
2. Zhu-Nakamura Theory
 - 2.1 Summary of the theory
 - 2.2 Landau-Zener type
 - 2.3 Nonadiabatic tunneling type
 - 2.4 Time-dependent version
 - 2.5 Other types of nonadiabatic transitions
3. Applications to Multi-Channel Problems
 - 3.1 Various problems and numerical applications

3.2 Control of molecular processes by external fields

4. Electronically Adiabatic Chemical Reactions

5. Electronically Nonadiabatic Chemical Reactions

5.1 New implementation of the TSH method by the Zhu-Nakamura theory

5.2 Charge transfer processes in the DH_2^+ system

6. Multi-Dimensional Tunneling

6.1 Three types of problems and effects of multi-dimensionality

6.2 Powerful theory for multi-dimensional tunneling

7. Future Perspectives

I-E-3 Analytical Solutions to Wave Packet Dynamics in a Laser Field**NAKAMURA, Hiroki**

Analytical solutions are obtained for the non-adiabatic transition between two linear potentials in coordinate space coupled by a time-dependent laser field within the framework of the dressed-state (or Floquet) representation. This can provide a basis for the analysis of wave packet dynamics in a chirped laser field.

I-F Quantum Dynamics of Chemical Reactions**I-F-1 Accurate Quantum Dynamics of Electronically Nonadiabatic Chemical Reaction in the DH_2^+ System****KAMISAKA, Hideyuki¹; BIAN, Wensheng;
NOBUSADA, Katsuyuki²; NAKAMURA, Hiroki**
*(¹GUAS; ²Hokkaido Univ.)**[J. Chem. Phys. **116**, 654 (2002)]*

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

I-F-2 Chemical Reactions in the $\text{O}(^1D) + \text{HCl}$ System I. *Ab Initio* Global Potential Energy Surfaces for the $1^1A'$, $2^1A'$, and $1^1A''$ States**NANBU, Shinkoh; KAMISAKA, Hideyuki¹; BIAN, Wensheng;
AOYAGI, Mutsumi²; TANAKA, Kiyoshi³; NAKAMURA, Hiroki**
*(¹GUAS; ²IMS and Kyushu Univ.; ³Hokkaido Univ.)**[J. Theor. Comp. Chem. in press]*

New global *ab initio* potential energy surfaces (PES) are presented for the low-lying $1^1A'$, $1^1A''$ and $2^1A'$ electronic states which are correlated to $\text{O}(^1D) + \text{HCl}$. These potential energy surfaces are computed by using the multi-reference configuration interaction method with the Davidson correction (MRCI+Q). The reference functions are constructed by the complete active space self-consistent field (CASSCF) calculations using the quadruple zeta + polarization basis set augmented with diffuse functions. The computations are carried out at about 5000 molecular conformations on each three-dimensional potential energy surface. The high accuracy of the computations is confirmed by a comparison with the available most accurate data for the ground state $1^1A'$; thus the present work is the first report of the accurate potential energy surfaces for the two excited states. Three low-lying transition states on the excited surfaces, two (TS2 and TS4) on $1^1A''$ and one (TS3) on $2^1A'$, are found. Since TS2 and TS3 are as low as 0.07 eV and 0.28 eV, respectively, and correlate to the $\text{OH}(^2\Pi) + \text{Cl}(^2P)$ product, these excited surfaces are expected to play quite important roles in the reaction dynamics. Possible effects of nonadiabatic couplings

among the three PESs are also briefly discussed, although the nonadiabatic couplings have not yet been estimated. The quantum reaction dynamics on these three PESs are discussed in the second accompanying paper.

I-F-3 Chemical Reactions in the O(1D) + HCl System II. Dynamics on the Ground $1^1A'$ State and Contributions of the Excited ($1^1A''$ and $2^1A'$) States

KAMISAKA, Hideyuki; NANBU, Shinkoh; BIAN, Wensheng; AOYAGI, Mutsumi¹; TANAKA, Kiyoshi²; NAKAMURA, Hiroki
(¹IMS and Kyushu Univ.; ²Hokkaido Univ.)

[*J. Theor. Comp. Chem.* in press]

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

I-F-4 Chemical Reactions in the O(1D) + HCl System III. Quantum Dynamics on the Excited ($1^1A''$ and $2^1A'$) Potential Energy Surfaces

KAMISAKA, Hideyuki; NANBU, Shinkoh; BIAN, Wensheng; AOYAGI, Mutsumi¹; TANAKA, Kiyoshi²; NAKAMURA, Hiroki
(¹IMS and Kyushu Univ.; ²Hokkaido Univ.)

[*J. Theor. Comp. Chem.* in press]

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

I-F-5 Use of Diabatic Basis in the Adiabatic-by-Sector R-Matrix Propagation Method in Time-Independent Reactive Scattering Calculations

MIL'NIKOV, G. V.¹; NAKAMURA, Hiroki
(¹IMS and Inst. Struct. Macrokinetics, Russia)

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

We propose a new recipe for the R -matrix propagation which combines the ideas of the adiabatic-by-sector (ABS) method and the sequential diagonalization/truncation technique. The R -matrix is determined in the adiabatic representation but the method does not require calculations of adiabatic channel functions at radial points inside the sector of propagation. This is a modification of the previously proposed ABS approach and can significantly reduce the computational time and memory in the energy independent part of scattering calculations. The code is checked by a test calculation of the reaction $O(^3P) + HCl \rightarrow OH + Cl$ using a LEPS potential energy surface (PES). The applicability of the method is further demonstrated by accurate quantum calculations of the endoergic reaction $H(^2S) + O_2(^3\Sigma_g^-) \rightarrow OH(^2\Pi) + O(^3P)$.

I-G Laser Control of Molecular Processes

I-G-1 Control of Photodissociation Branching Using the Complete Reflection Phenomenon: Application to HI Molecule

FUJISAKI, Hiroshi; TERANISHI, Yoshiaki¹; NAKAMURA, Hiroki
(¹IMS and JAERI)

[*J. Theor. Comp. Chem.* in press]

The laser control of photodissociation branching in a diatomic molecule is demonstrated to be effectively achieved with use of the complete reflection phenomenon. The phenomenon and the control condition can be

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

I-G-2 Control of Molecular Processes by a Sequence of Linearly Chirped Pulses

NAGAYA, Kuninobu¹; TERANISHI, Yoshiaki²;

NAKAMURA, Hiroki*(¹IMS and Univ. Sherbrooke; ²IMS and JAERI)*

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

I-G-3 Selective Excitation among Closely Lying Multi-Levels**NAGAYA, Kuninobu¹; TERANISHI, Yoshiaki²; NAKAMURA, Hiroki***(¹IMS and Univ. Sherbrooke; ²IMS and JAERI)*

[*Laser Control and Manipulation of Molecules* A. Bandrauk, R. J. Gordon and Y. Fujimura, Eds., ACS Symposium Series 821, American Chemical Society (2002)]

A new idea is proposed to accomplish selective and

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

I-G-4 Photodissociation of H₂⁺ and HD⁺ in an Intense Laser Field**KONDORSKIY, Alexey¹; NAKAMURA, Hiroki***(¹IMS and Lebedev Phys. Inst., Russia)*

The photodissociation of H₂⁺ and HD⁺ by an intense laser pulse is investigated by solving the close-coupling equations without discretization. For the case of H₂⁺ the photodissociation spectra are calculated under the condition mimicking the experimental one and a fairly good agreement with the experiment is obtained. The uncertainty in the relative phases of initial states is found to lead to somewhat of smoothing of the spectra, depending on the pulse length. It is also found that Raman type transitions via intermediate dissociation continuum play an important role in determining the photodissociation spectra. This leads to a population increase of lower vibrational states and deforms the spectral profile. Dissociation from the lower vibrational states due to the bond softening is not strong enough.

Photodissociation spectra and angular distribution are calculated also for HD⁺ under the same conditions as in the H₂⁺ case. The dipole transitions lead to additional structures in the energy spectra and angular distribution. There is a noticeable difference in the peak positions of dissociation spectrum for particles dissociated by the direct electronic dipole transition and by the transitions via intermediate bound states.

The photodissociation dynamics is further clarified by using the three-dimensional plots of the spectra as a function of the field intensity and frequency.

I-H Theory of Multi-Dimensional Tunneling**I-H-1 Practical Implementation of the Instanton Theory for the Ground-State Tunneling Splitting****MIL'NIKOV, G. V.¹; NAKAMURA, Hiroki***(¹IMS and Inst. Struct. Macrokinetics, Russia)*

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

The instanton theory is reformulated with use of the path integral approach and the Wentzel-Kramers-Brillouin approximation to the Schrödinger equation. Both approaches are shown to provide the same results. A new practically useful semiclassical formula is derived for the tunneling splitting of the ground state,

which can be implemented for high-dimensional systems. The theory is applicable to systems of arbitrary Riemannian metric and is also supplemented by a practical numerical recipe to evaluate the instanton trajectory, *i.e.*, periodic orbit, in multidimensional space. Numerical examples are presented for three-dimensional (3D) and 2D systems of HO₂ and malonaldehyde, respectively.

I-H-2 Instanton Theory for Multi-Dimension Decay through Tunneling**MIL'NIKOV, G. V.¹; NAKAMURA, Hiroki***(¹IMS and Inst. Struct. Macrokinetics, Russia)*

In our recent publication, we have formulated a practically efficient theory for the tunneling splitting of the ground state. The final result is applicable to large dimensional systems with an arbitrary metric system. The idea can be generalized to be applied to decay of a

metastable state through tunneling. An efficient method to find an instanton path and a canonically invariant expression of the decay rate can be formulated. The final result can be applied virtually to any high dimensional systems.

I-I New Methods for Scattering Calculations

I-I-1 Regularization of Scattering Calculations at *R*-Matrix Poles

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(¹IMS and Inst. Struct. Macrokinetics, Russia)

[*J. Phys. B: At., Mol. Opt. Phys.* **34**, 791 (2001)]

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

and the density of resonance states.

I-I-2 Calculation of Resonances via the *R*-Matrix Method

MIL'NIKOV, G. V.¹; NAKAMURA, Hiroki
(¹IMS and Inst. Struct. Macrokinetics, Russia)

Using the new spectral representation of Green's function previously proposed by us [*Comput. Phys. Commun.* **135**, 278 (2001)], we calculate the density of states and extract parameters of resonances in scattering system. The method is implemented for the resonances in *d* μ molecule below $\mu(n = 2)$ threshold.

I-J Theoretical Studies of Dissociative Attachment and Dissociative Recombination

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

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MIL'NIKOV, G. V.²; NAKAMURA, Hiroki
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[*Physica Scripta.* **65**, 328 (2002)]

The new method of calculation of scattering Green's function recently proposed by the authors (G. V. Mil'nikov, H. Nakamura and J. Horáček, *Comput. Phys. Commun.* **135**, 278 (2001)) is applied to the process of dissociative attachment of low-energy electrons to HI molecule previously considered by Horáček, Domcke and Nakamura (*Z. Phys. D* **42**, 181(1997)). The calculation is extended to vibrationally and rotationally excited targets gas molecules. The temperature dependence of the dissociative attachment cross section is determined.

I-J-2 Analytical Treatment of the *K*-Matrix Integral Equation in the Dynamics of Superexcited Molecules

PICHL, Lukas¹; HIYAMA, Miyabi²; NAKAMURA, Hiroki

(¹Aizu Univ.; ²Univ. Tokyo)

Superexcited states (SES) constitute one peculiar class of electronically highly excited states of molecules whose internal energies exceed the corresponding lowest ionization potentials. They play important roles in various fields of chemistry and physics as intermediate states of dynamic processes. It is crucial to understand the characteristics of the central SES in order to systematically comprehend the various dynamic processes. Dissociative recombination represents one of good typical examples. According to the difference in the autoionization mechanisms the SESs are classified into the following two kinds: (i) multiply or inner-shell excited state, which is called "SES of the first kind," and (ii) rovibrationally excited Rydberg state, which is called "SES of the second kind." The dynamics of SES are governed by the two basic interactions: the electronic coupling $V(R, \epsilon)$ between the first kind of SES and the electronic continuum, and the quantum defect function $\mu(R)$, where R is the internuclear distance and ϵ is the electron energy. If these two quantities are available together with the potential curves $E_d(R)$ of the first kind of SES, then the MQDT (multi-channel quantum defect theory) presents a very powerful tool to investigate the various dynamics. These quantities should be basically evaluated by quantum chemical electronic structure theory, but it is not easy generally to obtain accurate

absolute values, unfortunately, especially in the case of $V(R, \epsilon)$. It is crucial to use spectroscopic experiments to improve the information. In this sense the interplay among quantum chemistry, dynamics theory, and experiment is very important. There is still one theoretical obstacle in this procedure. That is the solution of the K -matrix singular integral equation. The first order perturbation theory or the grid method is usually employed; but they are not accurate enough or not efficient enough. Here we present a new method which enables us to deal with the equation even analytically. Finally, when non-adiabatic transitions at potential curve crossings are to be analyzed, for instance in order to find out the final state branching in dissociative recombination, the compact and accurate Zhu-Nakamura theory can be used instead of the Landau-Zener formula.

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

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

I-K-1 Probing a Colored-Noise Induced Peak of a Strongly Damped Brownian System by One- and Two-Dimensional Spectroscopy

SUZUKI, Yoko; TANIMURA, Yoshitaka

[*Chem. Phys. Lett.* **358**, 51 (2002)]

When dynamics of a system strongly coupled to a white-noise environment is overdamped, in linear spectroscopy, the spectrum is observed as one peak near zero vibrational frequency. We found, however, that if the noise induced by the environment is colored and its correlation time is long, there is an additional peak at a frequency different from the system. We study the multi-dimensional spectrum, to observe the interplay between the overdamped motion and the weakly damped motion induced by the colored noise. Finally, we discuss the connection between the peak due to the colored noise and the Boson peak found in glass materials and supercooled liquids.

I-K-2 Vibrational Spectroscopy of a Harmonic Oscillator System Nonlinearly Coupled to a Heat Bath

KATO, Tsuyoshi; TANIMURA, Yoshitaka

[*J. Chem. Phys.* **117**, 6221 (2002)]

Vibrational relaxation of a harmonic oscillator nonlinearly coupled to a heat bath is investigated by the Gaussian-Markovian quantum Fokker-Planck equation approach. The system-bath interaction is assumed to be linear in the bath coordinate but linear plus square in the system coordinate modeling the elastic and inelastic relaxation mechanisms. Interplay of the two relaxation processes induced by the linear-linear and square-linear interactions in Raman or infrared spectra is discussed for various system-bath couplings, temperatures and correlation times for the bath fluctuations. The one-quantum coherence state created through the interaction with the pump laser pulse relaxes through different pathways in accordance with the mechanisms of the system-bath interactions. Relations between the present theory, Redfield theory and stochastic theory are also discussed.

I-K-3 Two-Dimensional Raman and Infrared Vibrational Spectroscopy for a Harmonic Oscillator System Nonlinearly Coupled with a Colored Noise Bath

KATO, Tsuyoshi; TANIMURA, Yoshitaka

[*J. Chem. Phys.* submitted]

Higher-order vibrational response functions of a harmonic oscillator are reconsidered by assuming a nonlinear coupling with a heat-bath from a quantum Fokker-Planck equation approach. In addition to a conventional linear-linear (LL) system-bath interaction, we consider a square-linear (SL) interaction in a Brownian oscillator model. The LL interaction yields vibrational energy relaxation, while the SL interaction mainly yields phase relaxation. The dynamics of a harmonic system are investigated by numerically integrating the Gaussian-Markovian Fokker-Planck equation under the condition of a colored and strong system-bath fluctuation, where the conventional perturbative approach cannot be applied. The response functions for the fifth-order nonresonant Raman and the third-order infrared (or equivalently the second-order infrared and the seventh-order nonresonant Raman) processes are calculated under the various combination of the LL and SL coupling strength. Results of two-dimensional response demonstrate that this spectroscopic technique is very sensitive to the mechanism of system-bath coupling and the correlation time of bath fluctuation; the signals exhibit echolike peak both in the fifth-order Raman and the third-order IR case, if the SL coupling is strong and the bath fluctuation is slow. We discuss the primary optical transition pathways involved in two-dimensional spectroscopy to study the echolike behavior. The optical pathways of the fifth-order Raman response from an "anisotropic" medium are newly found which were predicted by neither the weak system-bath coupling theory nor the conventional Brownian harmonic oscillator model.

I-K-4 Two-Time Correlation Function of a Two-Dimensional Quantal Rotator in a Colored Noise

SUZUKI, Yoko; TANIMURA, Yoshitaka

[*J. Phys. Soc. Jpn.* **71**, 2414 (2002)]

We study an absorption spectrum of a two-dimensional rotator coupled to a colored harmonic-oscillator bath. The absorption spectrum is analytically calculated from the generating functional of a reduced density matrix element for the rotator degrees of freedom. In the previous letter,¹⁾ the analysis of spectrum is limited to a white noise case. In this paper, we extend our theory to a colored noise case. We present the spectra for different temperatures, damping strength, and the correlation time of the noise. For a weakly damped rotator, at low temperatures, the spectra are sensitive to the system

dynamics that is determined by the quantization of the rotational motion. Such a quantized rotational motion depends on the noise effects. Hence we observe the peak shifts by the noise correlation time. For a strongly damped rotator, we find the bimodal spectrum in the slow modulation case. One of the peaks is caused by the effect of the colored noise, which does not appear in the case of the white noise. This peak is related to a librational motion induced by the coupling between the system and the bath oscillators with the near zero frequencies.

Reference

- 1) Y. Suzuki and Y. Tanimura, *J. Phys. Soc. Jpn.* **70**, 1167 (2001).

I-K-5 Energy-Level Diagrams and Their Contribution to Two-Dimensional Spectroscopic Signal: Distinction between Relaxation Mechanisms by Two-Dimensional Spectroscopy

OKUMURA, Ko¹; TANIMURA, Yoshitaka
(¹*Ochanomizu Univ.*)

We develop explicit Feynman rule for energy-level diagram or the corresponding physical processes in the Liouville space. Thereby we completely identify such diagrams and processes contributing to the two-dimensional response function in the Brownian oscillator model. We classify such diagrams or processes in quartet and numerically present signal separately from each quartet of diagrams or Liouville-space processes. We find that signal from each quartet is distinctly different from the others; we can identify each peaks in frequency domain with a certain quartet. This offers the basis for analyzing and assigning actual two-dimensional peaks and suggests the possibility of Liouville-space-path selective spectroscopy. As an application and also as a demonstration we present an example in which two familiar homogeneous mechanisms of relaxation are distinguished by existence or non-existence of certain peaks on the two-dimensional map; appearance or disappearance of certain peak is sensitive to the coupling mechanism. We also comment on some controversy on the result of a response function in the bilinear Brownian oscillator model.

I-K-6 Two-Dimensional Spectroscopy for a Two-Dimensional Rotator Coupled to a Gaussian-Markoffian Noise Bath

SUZUKI, Yoko; TANIMURA, Yoshitaka

The dynamics of a system in the condensed phase

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

I-K-7 Absorption Spectra for Two-Dimensional Rotator with Nonlinear System-Bath Coupling

SUZUKI, Yoko; TANIMURA, Yoshitaka

We investigate the relaxation process in a two-dimensional rotator system nonlinearly coupled to a harmonic heat bath with the use of the perturbation theory. In the previous works, we restricted our study to the linear-linear coupling between the system and the bath and obtained the continuous spectra. However, in the many realistic problems, the absorption spectra show discrete lines. To take into account experiments, we assume the system-bath interaction to be linear in the bath coordinate but the periodic function in the system coordinate. Using this coupling, we derive the absorption spectra of the rotator system which relates to a two-time correlation function of the dipole moment.

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

We investigate quantum dynamics of molecules or atom in condensed phases by means of various statistical physics approaches involving Monte Carlo method for a reduced density matrix. Effects of dissipation on a spin system, proton tunneling and electron transfer processes are investigated and compared with the classical dynamics.

I-L-1 The Energy Landscape for Solvent Dynamics in Electron Transfer Reactions: A Minimalist Model

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(¹Univ. Estadual Paulista; ²Univ. California, San Diego)

[*J. Chem. Phys.* **117**, 2172 (2002)]

Energy fluctuations of a solute molecule embedded in a polar solvent are investigated to depict the energy landscape for solvation dynamics. The system is modeled by a charged molecule surrounded by two layers of solvent dipolar molecules with simple rotational dynamics. Individual solvent molecules are treated as simple dipoles that can point toward or away from the central charge Ising spins. Single-spin-flip Monte Carlo kinetics simulations are carried out in a two-dimensional lattice for different central charges, radii of outer shell, and temperatures. By analyzing the density of states as a function of energy and temperatures, we have determined the existence of multiple freezing transitions. Each of them can be associated with the freezing of a different layer of the solvent.

I-L-2 A Quantum Master Equation with a Langevin Force; a Realization of a Real-Time Quantum Monte-Carlo Simulation in a Dissipative Environment

TANIMURA, Yoshitaka

A reduced description of a two-level system for a spin-Boson system in a functional integral form is considered. The thermal activation term in the Feynman-Vernon influence functional is expressed as a contribution from a Langevin force with use of an auxiliary function with Gaussian probability distribution. A quantum master equation with the Langevin force, which is valid at any bath temperature without using a rotating wave approximation, is deduced by constructing the finite difference expression of the density matrix elements. The equation amenable to carry out a real-time Monte Carlo simulation, since in addition to a damping term, it contains an external random force. The temperature effects are taken into account through the correlation function of the random force, which is related with the damping term through the fluctuation-dissipation theorem. Trajectories of a quantum random walk numerically generated by solving the equation are presented and discussed.

I-M Theoretical Studies of Correlated Electron Systems

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

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

HINO, Osamu¹; TANIMURA, Yoshitaka; TEN-NO, Seiichiro²
(¹Univ. Florida; ²Nagoya Univ.)

[*J. Chem. Phys.* **115**, 7865 (2001)]

A biorthogonal formulation is applied to the non-Hermite transcorrelated Hamiltonian, which treats a large amount of the dynamic correlation effects implicitly. We introduce biorthogonal canonical orbitals diagonalizing the non-Hermitian Fock operator. We also formulate many-body perturbation theory for the trans-

correlated Hamiltonian. The biorthogonal self-consistent field followed by the second order perturbation theory are applied to some pilot calculations including small atoms and molecules.

I-M-2 Application of the Transcorrelated Hamiltonian to the Linearized Coupled Cluster Singles and Doubles Model

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(¹Univ. Florida; ²Nagoya Univ.)

[*Chem. Phys. Lett.* **353**, 317 (2002)]

Explicitly correlated calculations using the trans-

correlated Hamiltonian are performed at the level of linearized coupled cluster (LCC) theory. Two different reference functions are employed in the calculations and the results are compared with those of the conventional LCC. The application to the water molecule shows a markedly better convergence of the correlation energies when the transcorrelated Hamiltonian is used than in the conventional approach. We also present results for some other ten-electron systems, Ne, HF, NH₃, and CH₄.

I-N Electronic Properties of Nanostructured Materials

I-N-1 Carbon Foam: Spanning the Phase Space between Graphite and Diamond

UMEMOTO, Koichiro¹; SAITO, Susumu^{1,2};
BERBER, Savas³; TOMÁNEK, David^{1,3}
(¹Tokyo Inst. Tech.; ²IMS and Tokyo Inst. Tech.;
³Mishigan State Univ.)

[*Phys. Rev. B* **64**, 193409 (2001)]

We study an unusual class of carbon structures, based on rigidly interconnected segments of graphite. The resulting foamlike systems cover the structural phase space extending from hexagonal diamond to graphite. Related to the most stable phases of carbon, these hybrid systems show an unusually high structural stability at low mass densities. Our density-functional calculations indicate that carbon foam is metallic, stable, and structurally rigid.

I-N-2 Electronic Structure of Ba₄C₆₀ and Cs₄C₆₀

UMEMOTO, Koichiro¹; SAITO, Susumu^{1,2}
(¹Tokyo Inst. Tech.; ²IMS and Tokyo Inst. Tech.)

[*Am. Inst. Phys. Conference Proc.* **590**, 305 (2001)]

We study the electronic structure of body-centered-orthorhombic Ba₄C₆₀ superconductor and Cs₄C₆₀. In both fullerenes, it is found that the band structure is metallic and that the low symmetry of the lattice gives rise to the lifting of the threefold degeneracy of *t_{1u}* and *t_{1g}* bands even at the Γ point. We study also the electronic structure of Cs₄C₆₀ under pressure and find it to be a promising candidate of a superconducting Cs fulleride.

I-N-3 Geometric and Electronic Structure of New Carbon-Network Materials: Nanotube Array on Graphite Sheet

MATSUMOTO, Takanori¹; SAITO, Susumu^{1,2}
(¹Tokyo Inst. Tech.; ²IMS and Tokyo Inst. Tech.)

[*J. Phys. Soc. Jpn.* **71**, 2765 (2002)]

We design a new class of carbon network materials with a periodically modified graphite sheet. The modified part corresponds to (6,6) carbon nanotube geometry. Their tube parts form triangular lattice on graphite sheet. On these systems each tube has six heptagons at the bottom, giving rise to a seamless *sp*²-C network with a negative curvature. We consider these nanotube arrays on graphite sheet with three kinds of tube-end geometries and various sizes for both graphite and tube parts. We report their electronic structure obtained by using a realistic tight-binding model, and for selected systems the density-functional theory. Interestingly, results show that most of them are semiconductors although both (6,6) tube and graphite are metallic. The difference in their tube-end geometries

and the sizes of graphite and tube parts affect their electronic structures. Some have nearly flat band states around the Fermi level, showing a possibility of ferromagnetic behavior if hole or electron is doped. Some are direct-gap semiconductors whose interband transition is optically allowed. Their typical gap energies are about 1 eV. Therefore they should emit infrared light.

I-N-4 First Principles Study of H₂ and CH₄ Physisorption on Carbon Nanotubes

AKAI, Yoshio¹; SAITO, Susumu^{1,2}
(¹Tokyo Inst. Tech.; ²IMS and Tokyo Inst. Tech.)

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

We study the energetics of physisorption of H₂ and CH₄ molecules on the single-walled carbon nanotube (SWNT) using the local density approximation in the framework of the density-functional theory. The radius of the studied nanotube is 4.69 Å, around the average size of the mass-produced SWNTs. Both inside and outside-wall physisorption processes with various molecular directions and adsorption sites are studied, and compared to those on a flat graphite sheet. It is found that H₂ and CH₄ molecules are generally stably adsorbed on the inside wall as well as on the outside wall. The energy gain upon physisorption of the H₂ on the inside wall of a carbon nanotube is about 0.10 eV, while that of CH₄ is about 0.17 eV. For the CH₄ adsorption, the energy gain depends considerably on a molecular direction. H₂ molecule is also stably adsorbed on the interstitial channel (IC) of the nanotube bundle, and the energy gain is about 0.19 eV. The Adsorption-site dependence is strong in the case of the H₂ adsorption on the outside wall of a nanotube and on the IC of nanotube bundles.

I-O Simulation and Dynamics of Chemical Systems

I-O-1 Quasi-Degenerate Perturbation Theory with General Multiconfiguration Self-Consistent Field Reference Functions

(¹Univ. Tokyo; ²IMS and Univ. Tokyo)

[*J. Chem. Phys.* **116**, 8270 (2002)]

NAKANO, Haruyuki¹; UCHIYAMA, Ryoma¹;
HIRAO, Kimihiko²

(¹Univ. Tokyo; ²IMS and Univ. Tokyo)

[*J. Comput. Chem.* **23**, 1166 (2002)]

The quasi-degenerate perturbation theory (QDPT) with complete active space (CAS) self-consistent field (SCF) reference functions is extended to the general multiconfiguration (MC) SCF references functions case. A computational scheme that utilizes both diagrammatic and sum-over-states approaches is presented. The second-order effective Hamiltonian is computed for the external intermediate configurations (including virtual or/and core orbitals) by the diagrammatic approach and for internal intermediate configurations (including only active orbitals) by the configuration interaction matrix-based sum-over-states approach. The method is tested on the calculations of excitation energies of H₂O, potential energy curves of LiF, and valence excitation energies of H₂CO. The results show that the present method yields very close results to the corresponding CAS-SCF reference QDPT results and the available experimental values. The deviations from CAS-SCF reference QDPT values are less than 0.1 eV on the average for the excitation energies of H₂O and less than 1 kcal/mol for the potential energy curves of LiF. In the calculation of the valence excited energies of H₂CO, the maximum deviation from available experimental values is 0.28 eV.

I-O-2 A Highly Efficient Algorithm for Electron Repulsion Integrals over Relativistic Four-Component Gaussian-Type Spinors

YANAI, Takeshi¹; NAKAJIMA, Takahito¹;
ISHIKAWA, Yasuyuki¹; HIRAO, Kimihiko²

(¹Univ. Tokyo; ²IMS and Univ. Tokyo)

[*J. Chem. Phys.* **116**, 10122 (2002)]

A highly efficient computational scheme has been proposed for the Dirac-Hartree-Fock and the Dirac-Kohn-Sham solutions using the generally contracted kinetically balanced Gaussian-type spinors. Nevertheless, the calculations based on the full Dirac Hamiltonian are limited to small systems if they contain heavy elements. The bottleneck is the calculation of the two-electron repulsions over the four-component GTs. The present study presents an improved algorithm for evaluation of the four-component relativistic integrals.

I-O-3 Accurate Relativistic Gaussian Basis Sets Determined by the Third-Order Douglas-Kroll Approximation with a Finite-Nucleus Model

NAKAJIMA, Takahito¹; HIRAO, Kimihiko²

Highly accurate Gaussian basis sets with a finite-nucleus model are developed for the 103 elements from H to Lr. The present GTO sets augment the relativistic basis sets with a point-charge model proposed in the previous paper of this series. The relativistic third-order Douglas-Kroll approach is adopted in optimizing the orbital exponents of a basis set by minimizing the atom self-consistent field energy. The basis sets are designed to have equal quality and to be appropriate for the incorporation of relativistic effects.

I-O-4 A Density Functional Study of van der Waals Interactions

KAMIYA, Muneaki¹; TSUNEDA, Takao¹; HIRAO, Kimihiko²

(¹Univ. Tokyo; ²IMS and Univ. Tokyo)

[*J. Chem. Phys.* **117**, 6010 (2002)]

The applicability of density functional theory (DFT) to van der Waals (vdW) calculations are investigated by using the long-range exchange correction scheme and the Andersson-Langreth-Lundqvist vdW functional. By calculating bond energy potentials of rare-gas dimers, it was found that the present scheme gives much more accurate potentials for all dimers than conventional sophisticated DFT methods do. We therefore confirmed that vdW bonds are constructed under the balance of long-range exchange and vdW correlation interactions, although neither of these interactions are usually contained in pure exchange-correlation functionals. It was also found that calculated vdW potentials are obviously affected by functional forms for rapidly varying densities. Especially in vdW calculations, we must employ a correlation functional that satisfies the fundamental condition for rapidly varying density.

I-P Theoretical Studies of Quantum Effects in Chemical Reactions

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

I-P-1 Quantum Scattering Calculations of the $O(^1D) + N_2(X^1\Sigma_g^+) \rightarrow O(^3P) + N_2(X^1\Sigma_g^+)$ Spin-Forbidden Electronic Quenching Collision

TAKAYANAGI, Toshiyuki
(JAERI and IMS)

[*J. Phys. Chem. A* **106**, 4914 (2002)]

Three-dimensional quantum scattering calculations have been carried out for the $O(^1D) + N_2 \rightarrow O(^3P) + N_2$ spin-forbidden electronic quenching process using a simplified collision model, in which only the lowest singlet surface and one triplet surface are taken into account. The standard close-coupling technique has been used to obtain nonadiabatic transition probabilities and the coupled-state approximation was applied to calculate the total quenching cross section. The results of the close-coupling calculations have been compared to the results of quasiclassical trajectory surface hopping method. It has been found that the trajectory surface hopping method give too large quenching probabilities compare to the quantum results, in which the quenching dynamics is exclusively resonance-dominated. Detailed analyses of the quantum results show that a curve crossing picture cannot be employed to describe the present nonadiabatic collision. The calculated quenching cross sections have been also compared to experimental data as well as previous theoretical results.

I-P-2 Translational Energy Dependence of NO + NO / $N_2 + O_2$ Product Branching in the $O(^1D) + N_2O$ Reaction: a Classical Trajectory Study on a New Global Potential Energy Surface for the Lowest $^1A'$ State

TAKAYANAGI, Toshiyuki¹; AKAGI, Hiroshi²
(¹IMS and JAERI; ²JAERI)

[*Chem. Phys. Lett.* **363**, 298 (2002)]

An analytical potential energy surface of the lowest singlet $^1A'$ state for the $O(^1D) + N_2O \rightarrow NO + NO / N_2 + O_2$ reaction has been developed on the basis of extensive ab initio electronic structure calculations at the CASPT2/cc-pVDZ level of theory within C_s constraint. A many-body expansion type function was employed to fit the calculated ab initio points. Classical trajectory calculations have been carried out using the newly developed potential energy surface. We found that the initial orientation angle significantly affect the NO +

NO / $N_2 + O_2$ product branching and the branching ratio decreases as the relative translational energy increases.

I-P-3 A CASPT2 Study of the Doublet Potential Energy Surface for the $CH(X^2\Pi) + N_2(X^1\Sigma_g^+)$ Reaction

TAKAYANAGI, Toshiyuki
(JAERI and IMS)

The $HCN_2 \rightarrow H + NCN(^3\Sigma_g^-)$ reaction, which is a key process in the $CH(^2\Pi) + N_2$ reaction mechanisms, has been studied using the ab initio electronic structure method at the CASPT2 level theory. First, we calculated two-dimensional potential energy surfaces as a function of two appropriate coordinates in order to understand overall mechanisms. Then, full-dimensional stationary point searches have been carried out using locally interpolated potential energy surfaces. Our calculations strongly support the recent proposal of Lin and co-workers that the $CH(^2\Pi) + N_2$ reaction does not yield spin-forbidden $N(^4S) + HCN$ products but yield spin-allowed $H(^2\Sigma) + NCN(^3\Sigma_g^-)$ products.

I-Q Electronic Structure of a Molecule in Solution

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

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

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

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

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

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

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

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

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I-Q-1 Equilibrium and Nonequilibrium Solvation Structure of Hexaamineruthenium (II,III) in Aqueous Solution: Ab Initio RISM-SCF Study

SATO, Hirofumi; HIRATA, Fumio

[*J. Phys. Chem. A* **106**, 2300 (2001)]

The electronic and solvation structures of the metal

complexes in aqueous solutions, $[\text{Ru}(\text{CH}_3)_6]^{2+}$ and $[\text{Ru}(\text{CH}_3)_6]^{3+}$, which are key species in electron transfer reactions, are studied by using RISM-SCF method. We have found that the effective charge on the ruthenium ion does not change so much on the process of oxydation, and the electron is lost mainly from the ligand groups.

The electrical potential fluctuations around these complexes are nicely described within a linear-response regime, though some nonlinear effect is observed.

I-R Solvation Thermodynamics of Protein and Related Molecules

Concerning biomolecules such as protein, it is a final goal for the biochemistry and biophysics to explore the relation between conformations and biological functions. The first important step toward the goal would be to explain the conformational stability of biomolecules in terms of the microscopic structure of the molecules in

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

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

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I-R-1 Partial Molar Volumes and Compressibilities of Alkali-Halide Ions in Aqueous Solution: Hydration Shell Analysis with an Integral Equation Theory of Molecular Liquids

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[*J. Phys. Chem.* **106**, 7308 (2002)]

The partial molar volume and partial molar compressibility of alkali-halide ions in aqueous solution at infinite dilution are calculated based on the RISM-Kirkwood-Buff theory. The theoretical results are in qualitative agreement with the corresponding experimental data. The volume and compressibility values are decomposed into the volume-exclusion and electrostriction contributions. The volume exclusion effect

qualitatively determines the dependence of the partial molar volume on the ion size, while the electrostriction effect dominates in the size dependence of the partial molar compressibility. The partial molar volume and compressibility are further analyzed by using the hydration shell model which enables us to distinguish a contribution from each hydration shell. For the primary hydration shell, we can make contact with the classical models of ion hydration proposed by Frank-Wen and Samoilov. Water molecules in the immediate vicinity of an ion always give a negative contribution to its partial molar volume. The first hydration shell makes a negative contribution to the partial molar compressibility for the ions classified with the "positive hydration" in terms of Samoilov's model, and does the opposite contribution for those with the "negative hydration." The reason why the water structure around a negatively hydrated ion is more compressible is explained in terms of density fluctuations around the ions from a viewpoint of the Landau fluctuation formula for the thermodynamic response functions.

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

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

terms of response of the collective excitations in solvent to the solute displacement.³⁾

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

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I-S-1 Translational Diffusion and Reorientational Relaxation of Water Analyzed by Site-Site Generalized Langevin Theory

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(¹*Tech. Univ. München*)

[*J. Chem. Phys.* **116**, 2502 (2002)]

The translational and rotational diffusion coefficients and the dielectric spectrum of water at the ambient condition are calculated using the exponential memory model previously proposed by us. The translational diffusion coefficient is in good agreement with experiments and computersimulations. However, the rotational diffusion and dielectric relaxation of the present theory are about ten times as fast as those of experiments. In order to clarify the origin of the disagreement, the memory kernel is directly obtained from the molecular-dynamics simulation and compared with the exponential model. It is found that the long-time part of the memory kernel, which is not considered in the exponential model, is dominant in the rotational diffusion and the dielectric relaxation of water.

I-S-2 Interaction-Site Model Description of the Reorientational Relaxation of Molecular Liquids: Incorporation of the Interaxial Coupling into the Site-Site Generalized Langevin/Mode-Coupling Theory

YAMAGUCHI, Tsuyoshi; HIRATA, Fumio

[*J. Chem. Phys.* **117**, 2216 (2002)]

The reorientational relaxation of nonlinear molecules in liquids is treated using the site-site generalized

Langevin/mode-coupling theory. We found an inconsistency between the rank-1 reorientational correlation functions of different vectors on a molecule when the molecule is nearly planer. We show that it is because the coupling between the torque and the acceleration of different rotational modes is missing in the theory.

A modification of the theory is proposed to incorporate this coupling, and the inconsistency between the reorientational correlation functions is remedied by the modification. We also apply the modified theory to the reorientational motion of water. The rotational part of the memory function becomes greater compared with the conventional theory, and it approaches to that from the molecular dynamics simulation. The charge-current spectrum of water is also shown to be improved by the modification.

I-S-3 Collective Density Fluctuations and Dynamics of Ions in Water Studied by the Interaction-Site Model of Liquids

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(¹*Tech. Univ. München*)

[*Condens. Mat. Phys.* **4**, 261 (2001)]

The collective excitations in water are studied based on the interaction-site model of liquids. Three collective modes, extracted from a generalized Langevin equation combined with the RISM theory of liquids, are identified as an acoustic mode and two optical modes. The drag force exerted on ions in water is described in terms of the response of these solvent collective excitations to the perturbation of ions. The ion-size dependence of the drag force, which has been a central issue in physical chemistry for long time, is studied in molecular detail based on the novel approach.

I-T Developing Theories of Liquids and Liquid Mixtures

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

In what follows, we describe our challenges to explore new problems related to liquids and liquid mixtures. The

challenge inevitably includes methodological development in the statistical mechanics of liquids.

I-T-1 Buthanol-Water Mixture, Structure of *tert*-Butyl Alcohol-Water Mixtures Studied by the RISM Theory

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(¹Fukuoka Univ.)

[*J. Phys. Chem. B* **106**, 5042 (2002)]

We calculated the site-site radial distribution functions for binary mixtures of *tert*-butyl alcohol (TBA) and water over the whole range of TBA molar fraction. The description uses the reference interaction site model (RISM) integral equation theory in the dielectrically consistent approach of Perkyns and Pettitt (DRISM), and the closure approximation of Kovalenko and Hirata (KH) providing appropriate description for association of polar molecular species of density ranging from gas to liquid. We employed the extended simple point charge (SPC/E) model for water, and the optimized potential for liquid simulations (OPLS) force field for TBA. The partial radial distribution functions obtained for the TBA-water mixture are in qualitative agreement with those available from neutron diffraction experiments and molecular dynamics simulations. It is found that hydrogen bonds between all species are enhanced with rise of the TBA concentration. The tetrahedral-like network of hydrogen bonding in dilute TBA aqueous solution gradually turns into the zigzag-like structure for a high TBA concentration. In dilute aqueous solution, TBA molecules cluster by the hydrophobic methyl groups, whereas their hydroxyl groups are incorporated into the water hydrogen-bonding cage surrounding the TBA aggregate. In concentrated TBA, water as well as TBA molecules associate into the zigzag-like hydrogen-bonding chains. The present work shows that the RISM/KH theory is able to qualitatively predict the association structure of alcohol-water liquid mixtures.

I-T-2 Improvement of the Reference Interaction Site Model Theory for Calculating the Partial Molar Volume of Amino Acids and Polypeptides

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KOVALENKO, Andriy; HIRATA, Fumio**
(¹Kyoto Univ.; ²Ritsumeikan Univ.)

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

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

I-T-3 Description of a Polar Molecular Liquid in a Disordered Microporous Material with Activating Chemical Groups by a Replica RISM Theory

KOVALENKO, Andriy; HIRATA, Fumio

[*Condns. Mat. Phys.* **4**, 643 (2001)]

We develop a replica generalization of the reference interaction site model (replica RISM) integral equation theory to describe the structure and thermodynamics of a polar molecular liquid sorbed in a quenched disordered porous matrix including polar chemical groups. It provides a successful approach to realistic models of molecular liquids, and properly allows for the effect of a quenched disordered medium on the sorbed liquid. The description can be readily extended to a mobile liquid comprising a mixture of ionic and polar molecular species. The replica RISM integral equations are complemented by the HNC closure and its partial linearization, the KH closure. These approximations are adequate to ionic and polar molecular liquids. Closed expressions for the excess chemical potentials of the quenched-annealed system are derived. We extend the description to the case of soft core interaction potentials between all species of the quenched-annealed system, in which the liquid and matrix equilibrium distributions are characterized in general by two different temperatures. The replica RISM/KH-HNC theory is applied to water sorbed in a quenched matrix roughly modeling porous carbonaceous material activated with carboxylic (–COOH) groups. The results are in qualitative agreement with experiment for water confined in disordered materials.

I-T-4 Toward a Molecular Theory for the van der Waals-Maxwell Description of Fluid Phase Transitions

KOVALENKO, Andriy; HIRATA, Fumio

[*J. Theor. Comp. Chem.* in press]

We briefly review developments of theories for phase transitions of molecular fluids and mixtures, from semi-phenomenological approaches providing equations of state with adjustable parameters to first-principles microscopic methods qualitatively correct for a variety of molecular models with realistic interaction potentials. We further present the generalization of the van der Waals-Maxwell description of fluid phase diagrams to account for chemical specificities of polar molecular fluids, such as hydrogen bonding. Our theory uses the reference interaction site model (RISM) integral equation approach complemented with the new closure we have proposed (KH approximation), successful over a wide range of density from gas to liquid. The RISM/KH theory is applied to the known three-site models of water, methanol, and hydrogen fluoride, and qualitatively reproduces their vapor-liquid phase diagrams and the

structure in the gas as well as liquid phases, including hydrogen bonding.

Furthermore, phase transitions of water and methanol sorbed in nanoporous carbon aerogel are described by means of the replica generalization of the RISM approach we have developed. The changes as compared to the bulk fluids are in agreement with simulations and experiment. The RISM/KH theory is promising for description of phase transitions in various associating fluids, in particular, electrolyte as well as non-electrolyte solutions and ionic liquids.

I-U Neutral-Ionic, Dimerization and Photoinduced Phase Transitions and Their Dynamics in Mixed-Stack Organic Charge-Transfer Complexes

Mixed-stack organic charge-transfer complexes have columns of alternating donor and acceptor molecules. Neutral-ionic and dimerization phase transitions are observed in them. Since the dimerization was observed in some neutral compounds, importance of the long-range Coulomb interaction has been pointed out. In such compounds, transfer-modulating electron-lattice coupling is known to be strong. Then, the finite-temperature density-matrix renormalization-group method is used to show that such electron-lattice coupling also brings about dimerization in the neutral phase and that the transition becomes continuous then. The tetrathiafulvalene-*p*-chloranil (TTF-CA) complex, on the other hand, shows the discontinuous and simultaneous, neutral-ionic and dimerization phase transitions. It shows the photoinduced phase transition as well. We have solved the time-dependent Schrödinger equation to reproduce peculiarities found in time-resolved spectroscopy, such as a) the threshold intensity above which the transition takes place, b) the macroscopic coherent oscillations of neutral-ionic phase boundaries, and c) the quick loss of the second-harmonic-generation signal.

I-U-1 Finite-Temperature Phase Diagram of Mixed-Stack Charge-Transfer Complexes

YONEMITSU, Kenji

[*J. Phys. Chem. Solids* **63**, 1495 (2002)]

The mixed-stack organic charge-transfer complex, (BEDO-TTF)(Cl₂TCNQ), has shown a phase transition accompanied with a sharp drop in the magnetic susceptibility and with an increase in the intermolecular overlap, as the temperature is lowered. Here we theoretically consider the possibility for a phase transition from the ionic phase to a neutral phase, which is driven by charge-transfer fluctuations. Using finite-temperature density-matrix renormalization-group calculations for the one-dimensional extended Hubbard model with alternating potentials, we show that, with increasing transfer integral t , a transition from the neutral phase to the ionic phase is induced by spin fluctuations for small t , while another transition from the ionic phase to the neutral phase is induced by charge-transfer fluctuations for large t . Near the phase boundary, the free energy is easily lowered by dimerization of transfer integrals or by staggered magnetic field. Thus, a further transition is also possible to a dimerized nonmagnetic phase or to an antiferromagnetic phase at a lower temperature. In two dimensions, we expect that the effect of charge-transfer fluctuations is larger and that the transition to the dimerized nonmagnetic phase is suppressed.

I-U-2 Lattice and Magnetic Instabilities near the Neutral-Ionic Phase Transition of the One-Dimensional Extended Hubbard Model with Alternating Potentials in the Thermodynamic Limit

YONEMITSU, Kenji

[*Phys. Rev. B* **65**, 205105 (2002)]

The effects of dimerization causing the alternation of transfer integrals on the neutral-ionic phase transition are studied in the one-dimensional extended Hubbard

model with alternating potentials at half filling. The finite-temperature density-matrix renormalization-group method is used to treat the thermodynamic limit. In the ionic phase, the free-energy gain is proportional to $\delta^{4/3}$ with δ being the degree of dimerization even near the phase boundary at low temperatures. In the neutral phase, the free-energy gain is quadratic for small transfer integral far from the phase boundary, but it is nonlinearly enhanced near the boundary. Large transfer integrals make the gain faster than δ^2 , so that they facilitate dimerization. The dimerization in the neutral phase increases the ionicity and lowers the spin excitation energies. These lattice effects are in contrast to the effects of a staggered magnetic field. Relevance is discussed to recently observed dimerization in the neutral phase of ClMePD-DMeDCNQI.

I-U-3 Variation of Excitation Spectra in Mixed-Stack Charge-Transfer Complexes

YONEMITSU, Kenji

[*Phase Transitions* in press]

Local excitation spectra in different spin and charge channels are calculated in the one-dimensional extended Hubbard model with alternating energy levels at half filling for mixed-stack charge-transfer complexes. Near the boundary between the neutral and ionic phases, the electronic system is easily distorted by an additional term that reduces the symmetry and opens a gap. Alternating transfer integrals produce a nonmagnetic spin-Peierls phase; while staggered magnetic fields produce an antiferromagnetic phase. Both of them enhance the ionicity when they are introduced into the neutral phase near the boundary. Accordingly, these additional terms enhance low-energy spin excitations, although these excitations are suppressed when compared with those in the regular ionic phase. The regular ionic phase has a larger spectral weight in the local current channel than the neutral phase. This would imply that, in one dimension and if the lattice effect is negligible, the ionic phase has smaller activation energy in the electric conductivity near the boundary than the

neutral phase.

I-U-4 Dynamic Spin Correlations near Neutral-Ionic Phase Transitions

YONEMITSU, Kenji

[*Physica B* submitted]

Near the neutral-ionic phase transition in the one-dimensional extended Hubbard model with alternating potentials at half filling, the effects of alternating transfer integrals and a staggered magnetic field on the local spin excitation spectrum are studied by using the finite-temperature density-matrix renormalization-group method. In the neutral phase, the alternation increases the ionicity and lowers the spin excitation energies toward the ionic phase, while the staggered magnetic field does not modify the spectrum up to a critical field above which the system becomes ionic.

I-U-5 Thermodynamics of Neutral-Ionic and Ferroelectric Phase Transitions in the Two-Chain System

KISHINE, Jun-ichiro; LUTY, Tadeusz¹;
YONEMITSU, Kenji
(¹Tech. Univ. Wrocław)

It remains an open issue to clarify the microscopic mechanism of the neutral-ionic phase transition and the photo-induced ferroelectric phase transition in the mixed-stack organic charge-transfer complex, TTF-CA. Of particular importance is to grasp the microscopic origin that distinguishes the neutral-ionic phase transition from the ferroelectric phase transition. The order parameter of the former transition is the charge concentration on the electron donor and acceptor sites, while that of the latter transition is the electric dipole moment that may be related to the microscopic electric current accompanied with the time-reversal symmetry breaking. Starting with a phenomenological argument, we first study thermodynamics of these phase transitions and consider how the interplay of electron correlation, lattice degrees of freedom and dimensionality effects enter the problem. We apply the transfer integral method to a two-chain system with a thermodynamic potential with triple minima. Mapping the problem onto a tunneling Hamiltonian and diagonalizing it, we study the phase transitions upon changing temperature and other controllable parameters. Finally, we discuss the neutral-ionic and ferroelectric phase transitions.

I-U-6 Domain-Wall Dynamics after Photoexcitations near Neutral-Ionic Phase Transitions

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YONEMITSU, Kenji
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[*Phase Transitions* in press]

Real-time dynamics of domain walls between the

neutral and ionic phases just after photoexcitations is studied by fully solving the time-dependent Schrödinger equation for a one-dimensional extended Peierls-Hubbard model, not by relying on the adiabatic approximation. The unrestricted Hartree-Fock approximation is used for electrons, and the lattice displacements are treated classically. Three characteristic time scales are observed: rapid oscillation of ionicity owing to the local charge transfer; slow oscillation of lattice displacements; and even slower and collective motion of domain walls. Steady growth of a metastable domains is achieved after complicated competition of micro domains. The relevance to recently measured, time-resolved photoreflectance spectra in TTF-CA is discussed.

I-U-7 Variation Mechanisms of Ground-State and Optical-Excitation Properties in Quasi-One-Dimensional Two-Band Electron Systems

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[*Mol. Cryst. Liq. Cryst.* **379**, 467 (2002)]

We study i) the ground-state and optical-excitation properties of halogen-bridged binuclear metal complexes, which are known as MMX chain compounds, by the strong-coupling expansion for a one-dimensional two-orbital extended Peierls-Hubbard model, and ii) the dynamics of domain walls between the neutral and ionic phases in mixed-stack charge-transfer complexes, by solving the time-dependent Schrödinger equation for a one-dimensional extended Peierls-Hubbard model with alternating energy levels. We find in i) that competition between electron-electron and electron-lattice interactions and competition between short- and long-range interactions are both important for the electronic phase variation, and in ii) that charge and lattice dynamics immediately after photoexcitations is complex and not explained simply within the domino picture.

I-U-8 Photoinduced Dynamics of Ionicity near the Neutral-Ionic Phase Boundary in a One-Dimensional Extended Peierls-Hubbard Model

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[*Synth. Met.* submitted]

Dynamics of the ionicity after photoexcitations in mixed-stack charge-transfer complexes is numerically studied by using a one-dimensional extended Peierls-Hubbard model with alternating potentials at half filling. The time-dependent Schrödinger equation and the Newton equation are solved for the electronic and lattice parts, respectively. Fourier analysis is performed for the ionicity. During the photoinduced phase transition, slow components are dominant and very broad reflecting complex motion of domain walls and lattice displacements. After the transition, fast and slow oscillations are

clearly seen, which correspond to the electronic and lattice motion, respectively.

I-V Self-Doping, Nonlinear Excitations and Photoinduced Transitions between Charge and Lattice Ordered Phases of Metal Complexes

Halogen-bridged binuclear platinum complexes show a variety of electronic phases owing to competing kinetic energy, Coulomb repulsion, and electron-lattice coupling. When the ligand is pop, electrons are so localized that the perturbation theory from the strong-coupling limit works very well for the ground and optically excited states. When the halogen is iodine in addition, as the distance between the neighboring MM units increases by changing counter ions or by reducing pressure, a discontinuous transition takes place from the charge-density-wave phase to the charge-polarization phase. This has been explained theoretically. In those materials which show the pressure-induced transition, a photo-induced transition is observed in the hysteresis loop. The transition is, however, only from the charge-density-wave to charge-polarization phases. We have clarified its mechanism. a) The lowest-energy photoexcitation brings about inter-unit charge transfer only in the former phase. b) The high-energy photoexcitation in the latter phase transfers charge so locally that the former phase never proliferates.

I-V-1 Self-Doping Effect on the Mott Transition Accompanied with Three-Fold Charge Ordering in (DCNQI)₂Cu

KUWABARA, Makoto¹; YONEMITSU, Kenji;
OHTA, Hiroshi¹
(¹Kobe Univ.)

[*Synth. Met.* in press]

The commensurate state with three-fold lattice distortion in the insulating phase of (DCNQI)₂Cu is studied based on a two-band Peierls-Hubbard model by using the density-matrix renormalization-group method. With strong electron correlation among the *d* electrons, self-consistent lattice modulation strongly blocks the charge transfer between the π and *d* orbitals in order to keep the commensurability condition even when the π -*d* level difference is widely varied. A transition to an incommensurate phase requires a large deviation of the π -*d* level difference from the optimal case.

I-V-2 Spin Solitons in the Alternate Charge Polarization Background of MMX Chains

KUWABARA, Makoto¹; YONEMITSU, Kenji;
OHTA, Hiroshi¹
(¹Kobe Univ.)

[*APES'01 proc.* in press]

We study spin solitons in the alternate charge polarization background of the MMX chains, using the unrestricted Hartree-Fock approximation to a one-dimensional Peierls-Hubbard model. The effects of the electron-lattice coupling and the electron-electron interaction on the shape of the soliton are discussed.

I-V-3 Photoexcited States and Photoinduced Dynamics in Electronic Phases of MMX-Chain Systems

YONEMITSU, Kenji; MIYASHITA, Naoyuki¹;
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[*Synth. Met.* submitted]

In the one-dimensional two-band three-quarter-filled Peierls-Hubbard model for halogen-bridged binuclear metal complexes $R_4[\text{Pt}_2(\text{pop})_4\text{I}]_n\text{H}_2\text{O}$ with counter ion *R* and pop = P₂O₅H₂²⁻, a transition from the charge-density-wave phase to the charge-polarization phase is photoinduced, but the opposite process is not. Its origin is explained by considering differences in low-energy photoexcitations in the two phases and coherence of respective order parameters. The different dynamics is demonstrated by solving the time-dependent Schrödinger equation.

I-V-4 Electromodulation Spectra of Optical Absorption in One-Dimensional Strongly Correlated Systems

KUWABARA, Makoto¹; YONEMITSU, Kenji;
OHTA, Hiroshi¹
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[*Synth. Met.* submitted]

Electromodulation spectra of optical absorption in one-dimensional strongly correlated electron systems are theoretically investigated by numerically solving the time-dependent Hartree-Fock equation for the extended-Hubbard model coupled to a classical external vector potential. The calculated spectra are qualitatively in good agreement with experimental results for one-dimensional Mott insulators.

I-W Dimensional Crossovers in Electronic Phases and Their Excitation Spectra of Quasi-One-Dimensional Organic Conductors

In quasi-one-dimensional segregated-stack organic charge-transfer complexes with a quarter-filled band, (TMTTF)₂X and (TMTSF)₂X, variation of physical properties under physical or chemical pressure can be viewed as a dimensional crossover. At this particular band filling, the umklapp process is essential to the confinement of fermions and to the antiferromagnetic long-range order. The dimensional crossover is demonstrated also in charge-transfer excitation spectra by the finite-temperature density-matrix renormalization-group method. Electron correlation is so strong in the most conducting direction that electron motion is confined in this direction at low energies. The perpendicular motion takes place only incoherently. This explains the observed behavior that is reminiscent of the doped Mott insulators.

I-W-1 Dimensional Crossovers and Phase Transitions in Strongly Correlated Low-Dimensional Electron Systems: Renormalization-Group Study

KISHINE, Jun-ichiro; YONEMITSU, Kenji

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In this review article, we have described our recent achievement on dimensional crossovers and phase transitions from incoherent metallic phases, based on the two-loop level perturbative renormalization-group approach. As a canonical example, we first take up spin-density-wave phase transitions in the quasi-one-dimensional organic conductors (TMTTF)₂X and (TMTSF)₂X, and elucidate the nature of the transitions in terms of the dimerized quarter-filled Hubbard chains. Secondly, we discuss the novel superconductivity in the doped ladder system Sr_{14-x}Ca_xCu₂₄O₄₁ under high pressure, and analyze the superconducting transition from the incoherent metallic phase (spin gap metal phase) in terms of the weakly-coupled Hubbard ladders. Thirdly, motivated by the experimental findings of the crossover from an antiferromagnetic phase, Anderson localization phase, and a normal Fermi liquid phase upon Cu doping in a organic compound (DI-DCNQI)₂Ag_{1-x}Cu_x, we discuss interplay of randomness, electron correlation, and dimensionality effects in weakly-coupled half-filled Hubbard chains

with weak quenched random potentials. Finally we discuss some two-dimensional electron systems where the two-loop renormalization-group procedure is well defined and works.

I-W-2 Correlation-Induced Dimensional Crossovers of Charge-Transfer Excitations in Quasi-One-Dimensional Organic Conductors

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Applying the finite-temperature density-matrix renormalization-group method to the spinless fermion model on a two-leg ladder, we have calculated the dynamical structure factors for the local charge transfer processes along the chains and across the chains. The intra-chain excitation spectra are sensitive to the inter-chain transfer integral and the chemical potential, while the inter-chain excitation spectra are sensitive to the intra-chain electron correlation. These dynamical properties are due to the collective motions of fermions along the chains and the energy-dependent confinement of fermions in the chains. At low but finite energies, the effects of the increasing inter-chain transfer integral on the local charge-transfer spectra are similar to those of the chemical potential deviating from zero.

I-X Underlying Gauge Structure and Competing Orders in Underdoped Cuprate Superconductors

The key issue in theoretical understanding of the high-temperature cuprate superconductors is how to describe the low-density carriers coupled with competing infrared collective degrees of freedom originating from strong correlation inherent in the doped Mott insulators. Although realization of the *d*-wave superconducting ground state upon doping has been established both experimentally and theoretically, it still remains as a highly challenging problem to describe the low-energy contenders such as the flux phase, the antiferromagnetic phase, the stripe phase, and so on. Here, we take account of the contenders as much as possible. First, based on an SU(2) formulation of the *t*-*J* model, we consider a superconducting vortex, where the flux state is stabilized in its core, and propose its physical consequences. Then, as a next step, both flux and antiferromagnetic degrees of freedom are included.

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

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

I-X-2 Underlying SU(2) Gauge Structure and Hidden Staggered Flux State in the Lightly Doped Spin Liquid

KISHINE, Jun-ichiro

[*J. Phys. Chem. Solids* **63**, 1559 (2002)]

The staggered flux state, that enters the low-energy spectrum of the d -wave superconducting state in the lightly doped spin liquid systems is discussed, based on an SU(2) lattice gauge theory formulation of the t - J model. An appropriate gauge transformation to describe physical quantities such as staggered orbital currents is proposed. Using this gauge (physical gauge), the staggered orbital current correlation is computed and consistency with a Gutzwiller-projected Monte Carlo analysis is argued.

I-X-3 Coexistence of Staggered Flux and Antiferromagnetic States in Superconducting Vortices in the Lightly Doped Mott Insulator

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Based on an SU(2) lattice gauge theory formulation of the t - J model, we numerically studied electronic states inside superconducting vortices in the lightly

doped Mott insulator. Applying the Bogoliubov-de Gennes type formulation to the vortices in the system, we found that an antiferromagnetic state coexists with the staggered flux state for doping smaller than some critical concentration. This is the first finding of the coexistence of the resonating-valence-bond type on-bond singlets and the on-site spin degrees of freedom. Relevance of this finding to the recent NMR experiments on the vortex core states is argued.