RESEARCH ACTIVITIES I
Department of Theoretical Studies

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

Theories of the electronic structure of molecules have been extensively developed for last four decades. The theories are in some senses at a matured stage. However, there are plenty of challenging and practically important problems to be solved.

I-A-1 Generalization of the Coupled-Cluster Response Theory to Multireference Expansion Spaces; an Application of the Coupled-Cluster Singles and Doubles Effective Hamiltonian

Seiichiro TEN-NO, Suehiro IWATA, Sourav PAL *(Nat. Chem. Lab. India and IMS)* **and Debashis MUKHERJEE** *(Indian. Assoc. Cult. Sci.)*

[*Theor. Chem. Acc.* (Prof. Fukui's memorial issue), in press]

Employing separate cluster ansatz in time-independent and dependent wave-operators, the coupled-cluster (CC) response theory is generalized to the multireferecne expansion spaces. For state energies, this corresponds to the multireference secular problem with an arbitrary similarity transformed effective Hamiltonian, $\tilde{H} = \Omega^{-1}H\Omega$. The effective Hamiltonian can be generated via the size-extensive CC methods. And thus the states in the multireference linear response theory (MRLRT) maintain the core-extensive properties as in the usual CC ones. We have used the Gelfand unitary group basis of the spin-adapted configurations to construct the matrix of $\tilde{H}$ in the MR excitation space.

As a preliminary application, the CC singles and doubles effective Hamiltonian is applied to excitation and photo-ionization energies of the CH^+ and N_2 molecules, compared with experimental results and those from other numerical procedures including conventional CC linear response theory (CC-LRT), multireference and full configuration interaction (MRCI and FCI) methods. The numerical results indicate that the MRLRT reproduces valence- and external-excited states quantitatively, combining best features of the CC-LRT and MRCI.

I-A-2 Modified McMurchie-Davidson Method for the Calculation of the Two-Electron Integral and its Derivatives

Feiwu CHEN and Suehiro IWATA

In the McMurchie-Davidson(MD) method, the product of two Gaussian functions are expanded as a linear combination of Hermit Gaussians. In the original procedure, the expansion coefficients are calculated recursively starting from the zero-th order function. We have shown that these coefficients are expressed explicitly without invoking any recursive procedure. Thus, the evaluation of two-electron integrals for higher angular momentum functions becomes more efficient than the original MD method. The derivatives of the two-electron integral respected to the nuclear coordinates are also expressed explicitly. The present extension of the MD method is expected to be very useful both for direct methods and for parallel computations in the Master-Slave mode.

I-A-3 A New Perturbation Expansion for Solution of Higher Roots in Quasi-Degenerate Problems

Feiwu CHEN and Suehiro IWATA

Quasi-degenerate perturbation theory (QDPT) using effective Hamiltonian theory is one of the most important approaches in modern quantum chemistry and dates back to the early partitioning technique by Löwdin. Based on the partitioning technique, we have derived an energy expression for the higher roots, which has a similar form with the conventional non-degenerate perturbation expansion. With perturbation parameter λ, Hamiltonian matrix can be partitioned as follows

$$\begin{pmatrix} H^0_{PP}+V_{PP} & \lambda V_{PQ} \\ \lambda V_{PQ} & H^0_{QQ}+\lambda V_{QQ} \end{pmatrix}, H_{PP}=H^0_{PP}+V_{PP}, H_{PQ}=V_{PQ}, H_{QQ}=H^0_{QQ}+V_{QQ}$$

The size of H_{PP} is n, and the eigenvalues of H_{PP} are $\varepsilon_p^{(0)}$, $p = 1,2,\cdots,n$. After some manipulation, the perturbation expansion for the p-th eigenvalue $E(\lambda,p)$ is expressed as

$$E(\lambda,p)=\varepsilon_p^{(0)}+\frac{1}{\sum_{j=1}^{n}A_{jj}\left(\varepsilon_p^{(0)}\right)}\left[\sum_{i=1}^{n}\sum_{a}^{Q-space}\frac{A_i^a\left(\varepsilon_p^{(0)}\right)V_{ai}}{\varepsilon_p^{(0)}-\varepsilon_a^{(0)}}\lambda^2+\sum_{i=1}^{n}\sum_{a,b}^{Q-space}\frac{A_i^a\left(\varepsilon_p^{(0)}\right)V_{ab}V_{bi}}{\left(\varepsilon_p^{(0)}-\varepsilon_a^{(0)}\right)\left(\varepsilon_p^{(0)}-\varepsilon_b^{(0)}\right)}\lambda^3+\cdots\right]$$

where $A_{jj}(\varepsilon_p^{(0)})$is the cofactor of determinant $|H^0_{PP} + V_{PP} - \varepsilon_p^{(0)}I|$, and $A_i^a(\varepsilon_p^{(0)})$ is a variant of the same determinant with the i-th column replaced by the first n elements of the a-th column of matrix V_{PQ}. A uniqueness of this expansion is that it converges to any of p-th eigenvalue ($p \le n$), and that the re-diagonalization within the model space P is not required.

I-A-4 Photodetachment Cross Section of Anions

Feiwu CHEN, Takeshi TSURUSAWA and Suehiro IWATA

A method to evaluate the photodetachment cross section using L^2 basis set and conventional ab initio MO CI wave functions is developed. To augment the Gaussian type functions, we introduce a set of eigenfunctions of a particle-in-box potential (PIBF) to describe the excess electron as well as the ejected electron. We code a new integral calculation package, in which the molecular integrals for the mixed basis set of the Gaussian and PIBF are evaluated. To reduce the number of integrals to be evaluated, only the coulomb (gg'|kk') and exchange (gk|g'k') types of two-electron integrals are calculated, where g and g' stand for the Gaussian functions, and k and k' for PIBF. Under this limitation of the integrals, we introduce a series of the approximations for many-electron wave functions of the initial and final states. Since the role of the electron correlation in the wave functions of the anion (initial state) and of the neutral (final state after an electron ejection) is different, special cares should be taken in developing the approximations. Because we use the discrete k values for PIBF, the hybrid basis set is still a L^2 basis set. To evaluate the photodetachment cross section, we use the Stieltjes Imaging (Lanczos Recursive) method.

I-A-5 Iterative Method for Spectral Decomposition

Tsutomu IKEGAMI and Suehiro IWATA

A method for the spectral decomposition of a ket state $|\boldsymbol{v}>$ with respect to a set of eigen states of Hamiltonian H (or any hermitian operators) is developed. First, a Chebyshev series $T_n(H)|\boldsymbol{v}>$ is generated through a sequential operation of H on $|\boldsymbol{v}>$. From the Chebyshev series, $\exp(iHt)|\boldsymbol{v}>$ is evaluated approximately for several value of t. By taking an inner-product of $\exp(iHt)|\boldsymbol{v}>$ with the original $|\boldsymbol{v}>$, we obtain an auto correlation function for $|\boldsymbol{v}>$, whose Fourier transformation gives the spectral density. If $\exp(iHt)|\boldsymbol{v}>$ itself is Fourier-transformed, the eigen states are obtained as a function of energy (or the others depending on the hermitian operator). The method is applied for the vibrational state of the Morse potential, and both the discrete and the continuum states are well described. The method works also well for one-dimentional multi-state problems.

I-B Water Clusters and Their Complexes with Atomic Ions

I-B-1 Dipole-Bound and Interior Electrons in Water Dimer and Trimer Anions: Ab Initio MO Studies

Takeshi TSURUSAWA and Suehiro IWATA

[*Chem. Phys. Letters* **287**, 95-110 (1998)]

Two types of structures of water dimer and trimer anion are found in the ab initio molecular orbital study with an extensively diffuse basis set. The first type is the dipole-bound anion, and the excess electron is distributed exteriorly, or on the surface of water clusters. In the second type of dimer and trimer anions, the excess electron is internally trapped between two waters. The electron correlation contributes to stabilizing the latter anions. The calculated vertical detachment energies for both types of trimers are positive.

I-B-2 A New Form of Stable Excess Electron: {e}·(HO) bonds

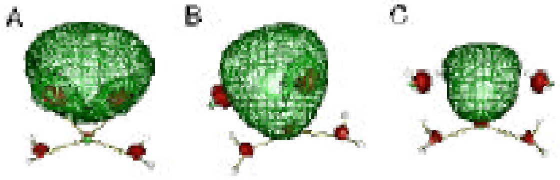
Takeshi TSURUSAWA and Suehiro IWATA

It has been known that two types of molecular anions are stable; one is dipole-bound anion and the other is valence anion. A typical example of the dipole bound anions is water dimer anion. The excess electron is trapped under the electrostatic field made by a dipole. The distribution of the excess electron is very diffuse and the detachment energy is very small. The other characteristics of the anion are that the geometric structure of the anion is nearly identical with that of the neutral. An example of the valence anions is C_2^- and $(CO_2)_2^-$. The excess electron occupies a bonding or non-bonding orbital. Contrary to the dipole-bound anion, the structure of the anion changes from that of the neutral species. While studying small water cluster anions, we have found a new form of excess electron. The electron is confined within a space surrounded by HO bonds of water molecules. Examples are interior type isomers of water dimer anion $(OH_2)\{e\}(H_2O)$ and trimer anions $\{e\}(H_2O)_3$; all water molecules being equivalent. A peculiarity of this form of anions is no direct hydrogen bonds between the water molecules surrounding the excess electron {e}. Therefore, after the photo-detachment the clusters of this form might be broken. One of the stable isomers of water tetramer anion has a form of $(OH_2)_2\{e\}(H_2O)_2$. In fact, the OH·{e}·HO structure is ubiquitous. In $(H_2O)_6^-$ and $(H_2O)_{12}^-$ studied by Kim's group, some of the isomers have the similar structure. Most importantly this form of anion is found in the ion pair state in metal-water clusters. The electron correlation contributes to stabilizing this form of anions. The calculated vertical detachment energies for this form is always positive.

I-B-3 Electronic Structure of $Li(H_2O)_n$ and $Na(H_2O)_n$ for n=3, 4 and 5

Takeshi TSURUSAWA and Suehiro IWATA

We have investigated the structures and the energies of $Li(H_2O)_n$ and $Na(H_2O)n$ for n = 3, 4 and 5 using *ab initio* MO method. The structures are optimized with the MP2/6-311++G(d,p) level of approximation. It turns out that both $Li(H_2O)_n$ and $Na(H_2O)_n$ can form similar structures and that the vertical ionization energies of the corresponding structures are almost independent of the metal atom included in the clusters. The main differences between the structures of $Li(H_2O)_n$ and $Na(H_2O)_n$ are the bond distance between the metal atom and oxygen atoms. R(Li-O) is about 1.9 Å and R(Na-O) is about 2.3Å. Although this difference is not small, its influence on the electronic and geometric structures are small. The structures of the isomers are classified to three types by the shape of the SOMO and its surrounding water molecules; '*internal*', '*semi-internal*' and '*surface*' types. This classification also corresponds to the classification by the vertical ionization energies (VIE); VIE of the *surface* is less than 3.4eV, VIE of *semi-internal* about 3.5eV and VIE of *internal* about 3.9eV. The *surface* (A), *semi-internal* (B) and *internal* (C) isomers of $Na(H_2O)_4$ are shown in Figure 1. In the figure 50% of the electron density in the singly occupied orbital (SOMO) is contained within a shaded bowl. The figures clearly indicate that the metal is fully ionized. The difference in the isomers is the electronic structure of the ejected electron {e} in SOMO. In *semi-internal* and *internal* types, the SOMO electron is surrounded by two water molecules as (HOH){e}-(HOH). The internal type becomes possible for $n \geq 4$. Indeed, Hashimoto et.al. showed in their paper that one of the isomers of $Li(H_2O)_n$ $n = 6$ and 8 have this structures.[1)] We conclude that the VIE of $M(H_2O)_n$ is determined mainly by the shape of the SOMO and its surrounding water molecules and not affected by the metal atom. The role of the alkali metal atom is only to make the base structure of larger cluster. Our theoretical finding may explain a mystery of the observed constant ionization threshold energy for all of $M(H_2O)_n$ (M=Li, K and Cs) of $n \geq 4$.



Reference:

1)K. Hashimoto and T. Kamimoto, *J. Am. Chem. Soc.* **120**, 3560 (1998).

I-B-4 Ab-Initio Monte Carlo Simulation Using Multicanonical Algorithm: Temperature Dependence of the Average Structure of Water Dimer

Pradipta BANDYOPADHYAY *(Grad. Univ. for Advanced Studies and IMS)*, **Seiichiro TEN-NO and Suehiro IWATA**

[*Molecular Physics* in press (1998)]

Theoretical studies of finite temperature effects on molecular spectra and properties are rare but extremely important. Ab-initio simulation techniques, though promising, suffer from the enormous computational cost to study the finite temperature effects. Multicanonical algorithm/reweighting technique is an efficient tool to study finite temperature effects. In this algorithm the system can explore any part of the potential energy surface with equal ease and get the reweighted canonical distribution for any temperature from only a single run making finite temperature studies computationally tractable. In this series of works the algorithm are combined with the ab initio MO calculations.

As a test example it was first applied to water dimer. The potential energies have been calculated at the RHF/6-31G* level of theory. Analysis of the radial and angular distribution functions show how with the increase of temperature thermally accessible states contribute to the average structure. With the increase of temperature structures, similar to the C_i transition state contributes considerably to the average structure.

I-B-5 Theoretical Assignments of the Photo-Dissociation Excitation Spectra of Mg^+ Ion Complexes with Water Clusters: Multi-Reference CI Studies

Hidekazu WATANABE *(Grad. Univ. for Advanced Studies, IMS and RIKEN)* **and Suehiro IWATA**

[*J. Chem. Phys.* **108**, 10078 (1998)]

With the ab initio multi-reference CI method, electronic excitation energies of $Mg^+(H_2O)_n$ clusters have been calculated in order to analyze the photo-dissociation excitation spectra reported by Fuke and his co-workers. Observed bands for $n \geq 2$ are assigned to the $s \rightarrow p$ transitions of the most stable isomer of $Mg^+(H_2O)_n$, with all waters directly bonded to the metal ion. For $n = 3$, 4 and 5, the dominant bands are also those of the most stable isomer, $[Mg^+(H_2O)_3](H_2O)_{n-3}$, which have three water molecules in the first hydration shell. There are, however, shoulders and weak peaks in the experimental spectra, and the calculations prove that these are due to the $s \rightarrow p$ transitions of less stable isomers. The calculated spectra clearly indicate the coexistence of a few isomers for $n \geq 3$ in molecular beam experiments.

I-B-6 Ab Initio MO Monte Carlo Simulation of $[X(H_2O)]^-$ (X = F, Cl , Br, I)

Katsuhiko SATOH and Suehiro IWATA

Theoretical study of hydrated anion clusters $[X(H_2O)_n]^-$ (X = F, Cl, Br, I, $n = 1$) has been performed using ab initio MO Monte Carlo simulation. The molecular dynamic simulation for these systems is sensitive to the quality of the potential energy. Experimentally the clusters have a thermal energy even under molecular beam conditions. It is thus necessary to examine the thermal effect based on the accurate potential energy. The MO calculation at each MC step is at the second-order Moller-Plesset (MP2) level with the 6-31+G** basis set. The statistical averages on structural properties are evaluated at the several temperatures to examine the dependence of temperature and of halides (F, Cl, Br and I). Ab initio vibrational frequencies and intensities are calculated for canonical ensembles. The spectra are compared with the recent experimental spectra.

I-C Structures and Vibrational Frequencies of Infinite Polymer Chains

I-C-1 Analytical Second Derivatives in Ab Initio Hartree-Fock Crystal Orbital Theory of Polymers

So HIRATA *(Grad. Univ. Adv. Stud. and IMS)* **and Suehiro IWATA**

[*J. Mol. Struct. (THEOCHEM)* **451**, 121 (1998)]

In the framework of ab initio Hartree-Fock crystal orbital theory of polymers, the formulas for the analytical second derivatives of energy with respect to in-phase (k = 0) nuclear coordinates are derived. The coupled perturbed Hartree-Fock (CPHF) equation is iteratively solved by using the direct (recomputation of two-electron integrals) atomic-orbital-based algorithm. Frequencies of the Brillouin zone center (k = 0) vibrations of all-*trans* polyethylene are calculated by using the STO-3G, 3-21G, and 6-31G* basis sets. The dependence of the frequencies on the number of neighbors included in the lattice summations, on the number of momentum sampling points in the first Brillouin zone, and on the convergence criterion for the CPHF solutions is examined. In our implementation, the use of analytical second derivatives is more efficient than the use of the finite differences of analytical first derivatives.

I-C-2 Analytical Energy Gradients in Second-Order Møller-Plesset Perturbation Theory for Extended Systems

So HIRATA *(Grad. Univ. for Advanced Studies and IMS)* **and Suehiro IWATA**

[*J. Chem. Phys.* in press (1998)]

The spin-restricted formulas for the analytical gradients of the second-order Møller-Plesset (MP2) perturbation energy are presented within the framework of ab initio crystal orbital theory of infinite one-dimensional lattices (polymers). The coupled perturbed Hartree-Fock equation for polymers is solved iteratively using the atomic-orbital-based algorithms. The MP2 energy and its gradient contributions are evaluated by the disk-based algorithms with the aid of the two-particle density matrix. The analytical-gradient method at the MP2 level as well as the analytical first- and second-derivative methods at the Hartree-Fock level is applied to calculate the equilibrium structures and harmonic vibrational frequencies of all-trans polyacetylene. The deviations of the calculated frequencies from the observed ones for the in-phase C=C stretching modes are reduced by about 70 % on going from HF/6-31G to MP2/6-31G theory.

I-C-3 Ab Initio Hartree-Fock and Density Functional Studies on the Structures and Vibrations of an Infinite Hydrogen Fluoride Polymer

So HIRATA *(Grad. Univ. Adv. Stud. and IMS)* **and Suehiro IWATA**

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

Structural parameters, binding energies, and frequencies of the infrared- and Raman-active vibrations are calculated for an infinite zigzag chain of hydrogen fluoride molecules by ab initio crystal orbital theory with the analytical energy gradient scheme. The Becke-Lee-Yang-Parr (BLYP), Becke3-Lee-Yang-Parr (B3LYP), and Hartree-Fock (RHF) levels are used in conjunction with the 6-311++G(d,p) basis set. Molecular orbital calculations at the BLYP, B3LYP, RHF, and the second-order Møller-Plesset perturbation (MP2) levels with the same basis set are carried out on linear HF oligomers containing up to six molecules, in order to examine the chain-length dependence of the energetic and structural properties. The predicted chain-length dependence is found significantly smaller in the RHF results than in the BLYP and B3LYP results. The RHF level substantially underestimates the downward frequency shifts in the intramolecular H-F stretching modes on going from the monomer to the polymer, while the shifts calculated at the BLYP and B3LYP levels are much closer to the experimental findings, although they are slightly overestimated. The RHF level strongly underestimates the intramolecular H-F bond length and overestimates the intermolecular F···H and F···F distances of the HF polymer, while the structural parameters predicted at the BLYP and B3LYP levels are in good agreement with the experimental results. It is concluded that the RHF level seriously underestimates the cooperative binding effects of consecutive hydrogen bonds, whereas the BLYP and B3LYP levels slightly overestimate this behavior; but these latter levels provide much better description than the former. Vibrational assignment of librational modes of HF crystals is reexamined on the basis of the calculated frequencies. The observed frequencies of the librational and pseudo-translational modes fall between the corresponding frequencies calculated at the RHF and density functional levels.

I-D Structures and Reations of Atomic and Molecular Clusters

I-D-1 Photodissociation Dynamics of Argon Cluster Ions

Tsutomu IKEGAMI and Suehiro IWATA

The photodissociation process of argon cluster ions is studied by using Tully's MDQT (molecular dynamics with quantum transition) method. It is demonstrated that the non-adiabatic transitions play an important role in the process. The lifetime of the initial photo-excited state and the recovery time to the electronic ground state are obtained for several cluster sizes and excitation energies. The decay curve of the photo-excited state is composed from the gaussian-like decay followed by an exponential decay. The initial gaussian-like delay of the decay may be attributed to the acceleration time of the nuclei. The number of the non-adiabatic transitions required for the recovery to the ground state increases with the excitation energy, while the rate of each transition decreases. As a result, the recovery to the ground state becomes faster for the lower excitation energy. The low rate at the higher excitation energy may be explained from the low density of states in the energy range.

I-D-2 Theoretical Investigation of the Structure and Spectroscopy of Silicon-Carbon Mixed Clusters

Pradipta BANDYOPADHYAY *(Grad. Univ. for Advanced Studies and IMS)*, **Seiichiro TEN-NO and Suehiro IWATA**

Pure Silicon and Carbon clusters have been studied extensively over the years both theoretically and experimentally. However, the same is not true for mixed Silicon-Carbon clusters. The mixed clusters demand interest not only because of its importance in material science but also because of the inherent complexity associated with its structures and spectra. It has been suggested that the complex photoelectron spectra of Silicon-Carbon anion clusters are due to the presence of several isomers at the experimental condition.1) In the present work mixed Silicon-Carbon clusters $Si_mC_n^-$ where $m + n = 4$ have been studied theoretically. Ab initio molecular orbital calculations at the CASSCF and MRCI level have been performed to determine the vertical detachment energies (VDE). It has been found that the VDEs are very much sensitive to the levels of electronic structure calculation. For $Si_2C_2^-$, the highly complex photoelectron spectra is presumably from the contribution of linear and ring structures. As enormous computational cost prohibits ab initio simulation with reliable electronic structure calculation for this system, the relative contributions of two structures have been evaluated by the quantum cluster equilibrium model.2)

References

1)A. Nakajima et. al., *J. Chem. Phys.* **103**, 2050 (1995).

2)F. Weinhold, *J. Chem. Phys.* **109**, 367 (1998).

I-D-3 Model Study of H-Bonded ROH $(NH_3)_5$ Clusters: A Search for Possible Ground-State Proton Transfer Species

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[*Chem. Phys. Letters* **292**, 87 (1998)]

Model studies have been made of the non-transferred (reactant) and proton-transferred (product) species of the ground-state hydrogen-bonded clusters $ROH(NH_3)_5$, where ROH is an aromatic alcohol. The structure, relative energies and vibrational frequencies of this species were obtained at the HF/6-31G* level of theory. It was found that proton transfer can proceed in the case of phenols with the electron-withdrawing substituents. A low-frequency vibration, which corresponds to the synchronous motion of the solvation shell, does exist in these clusters. The energy of the lowest π-π* transition is calculated for aromatic alcohols and their anions at the CASPT2 level with a VDZ basis set.

I-D-4 Ab Initio MO Studies of van der Waals Molecule $(N_2)_2$: Potential Energy Surface and Internal Motion

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[*J. Chem. Phys.* in press (1998)]

The equilibrium structure, potential energy and van der Waals (vdW) mode vibration of dimer of nitrogen molecule $(N_2)_2$ have been studied with high levels of ab initio calculations. The most stable structure is found to be a 45 degree canted parallel structure of C_{2h}. On the other hand, neither T-shape of C_{2v} nor cross shape of D_{2d} is a stable structure, but they are transition state structure, contrary to the previous calculations. The out-of-plane motion changing from the 45 canted parallel structure of C_{2v} to the cross shape of D_{2d} has a higher barrier than the in-plane motion. The binding energy of two N_2 molecules is about 80 cm^{-1} and the fundamental frequency of vdW stretching mode is estimated to be 22 cm^{-1}. A very small energy difference by 5 cm^{-1} between the C_{2h} and C_{2v} structures implies that two molecules move coherently like a gear rotation in the plane. This internal freedom of motion should make the rotational energy states extremely modulated, and therefore, a very complex spectral patter could be expected.

I-D-5 Theoretical Studies of Clusters of H_2 Molecules at High Pressure

Debasis MUKHOPADHYAY *(R. K. Mission Vidyamandira,*

India) **and Pradipta BANDYOPADHYAY** *(Grad. Univ. Adv. Stud. and IMS)*

Assemble of hydrogrn molecules at high pressure was predicted to form an atomic and presumably a metallic solid and this prediction has motivated experimental and theoretical studies over the years. We focused our attention on the observation of a dramatic (> 1000 fold) enhancement of the infrared (IR) intensity at the high pressure phase above 150 Gpa, characterized by a discontinuity of the vibrational frequency. It is noteworthy that Raman intensity shows only monotonic increase in this region. Such intense IR has been attempted to be explained by electron-vibration coupling to postulated charge-transfer (CT) states. In a recent study by Soos and Mukhopadhyay direct evaluation of the dipole derivative for overlapping H_2 dimer, with intermolecular distance corresponding to the pressure of 150 Gpa, has been seen to be consistent with the experimental IR oscillator strength, with hexagonal-close-packed lattice structure of molecular solid hydrogen. It was found that for a H_2 molecule with all its nearest neighbors, only one pair has important contribution. We take this dimer as 'good' dimer. In order to test the extensibility of the understanding within the dimer picture to the actual case of molecular solid, we have studied some fabricated structures obeying the geometry of the hcp lattice with ab initio MO methods. The MCSCF and closed shell HF wavefunctions are used. The models we have studied (I) n 'good' dimers oriented along z-axis for n = 2, 3, 4, (ii) a 'good' dimers with complete nearest neighbour environment, and (iii) two hexagonal planes of 7 pairs H_2 molecules, each dimer having orientation of the 'good' dimer. For case (i) we have dipole derivative consistently as n times that of the single 'good' dimer. Notably, extra interactions arising from the assembles are found to be not important. For case (ii) we have the dipole derivative of the order of magnitude of the 'good' dimer stripped of the neighbors. This is interesting, in particular, as here effective contribution from the interaction of the nearest neighbor molecules has seen to be negligibly small and practically null.

I-E Accurate Studies of Excited States of Small Molecules

I-E-1 A Theoretical Study of the Electronic Structure and Spectroscopic Properties of the Low-Lying Electronic States of the Molecule AlSi

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[*Chem. Phys.* **232**, 95 (1998)]

Twenty-one lowest-lying electronic states of the species AlSi are described theoretically using the internally contracted multi-reference configuration interaction approach and natural orbitals generated from a state-averaged density matrix. Correlated consistent valence quadruple-zeta (cc-pVQZ) atomic functions are used in the expansion of the one-electron basis. Potential energy curves are presented for all the states as well as a description of the electronic structure characterizing the most relevant ones. Dissociation and excitation energies, and dipole moment functions complete the electronic structure description. Solution of the radial nuclear equation allowed the determination of vibrational energies, and vibrational and rotational constants. For the ground state ($X^4\Sigma^-$), R_e = 2.424 Å and D_e = 2.53 eV. The first excited quartet is a $A^4\Delta$ located 2.29 eV (T_e) higher in energy, with a longer equilibrium distance (2.887 Å), and smaller, D_e, 0.24 eV. The first quartet directly accessible by a one-photon transition is the $B^4\Pi$ (T_e = 2.3l eV, R_e = 2.520 Å, D_e = 0.22 eV); the transitions $X^4\Sigma^-$ – $B^4\Pi$ are expected to fall in the green region of the visible spectrum. Higher-lying $^4\Pi$ states show very noticeable changes in the potential function due to avoided crossings. Within ~ 1.2 eV from the ground state there are located five doublet states; the lowest one a $^2\Sigma^-$. with T_e = 0.72 eV, R_e =2.415 Å, and D_e = 1.81 eV. For selected states, transition dipole moments, transition probabilities and radiative lifetimes are also presented. Crossings of various states and the energetic closeness of others are expected to play non-negligible perturbative effects in the spectra. The global picture of the electronic states presented will certainly be an important aid to experimentalists in the spectroscopic investigation of this species.

I-E-2 The Variety of [Fe,N,O] Isomers. A Theoretical Study

Andreas FIEDLER and Suehiro IWATA

[*J. Phys. Chem.* **102**, 3618 (1998)]

The stationary points on the potential energy hyper surfaces of triatomic [Fe,N,O] have been systematically studied using an economic combination of a density functional/Hartree Fock hybrid method, i.e. the B3LYP functional, and the multi-reference averaged quadratic coupled cluster approach. The global minimum is linear FeNO ($^2\Delta$) which is not adiabatically connected to the neutral ground state fragments Fe and NO. Side-on and oxygen bound isomers have low barriers for rearrangement, however, might be stabilized due to ligand effects. Inserted OFeN ($^4A''$) is kinetically stable although it lies considerably higher in energy than the other isomers. The calculations indicate near-degenerate ground states for all isomers. We discuss the implications for the reported experimental observations. Furthermore, the findings are rationalized using valence-bond and molecular-orbital theories.

I-E-3 Theoretical Studies of Highly-Excited Valence States of N_2^+ Molecule Ion

Kazutoshi OKADA *(Grad. Univ. for Advanced Studies)***, G. K. JARVIS** *(Iowa State Univ., U.S.A.)***, Cheuk Y. NG** *(Iowa State Univ., U.S.A.)* **and Suehiro IWATA**

Recently highly-excited valence states of nitrogen cation have been studied with synchrotron radiation source. In particular, the $C^2\Sigma_u^+$ state of N_2^+ has been examined with various types of photoelectron spectra. In the present studies, we have calculated the accurate potential energy curves of the doublet and quartet states lying 90,000 cm^{-1} above the zero vibrational level of the ground state $X^2\Sigma_g^+$. The basis set used in the multi-reference configuration interaction (MRCI) calculations is [5111/211/21/2]. The calculated dissociation energy D_0 of the neutral molecule is > 9.5eV, and is very close to the experimental energy (9.754 eV). The error in the excitation and ionization energies at the dissociation limit is also within 200 cm^{-1}. The accurate description near the dissociation limit for the $B^2\Sigma_u^+$ state is required in the present purpose, because its highly-lying vibronic levels is expected to interact with the vibronic levels of the $C^2\Sigma_u^+$ state. Vibrational and rotational levels for each electronic state are calculated with our FEM1D program. In our calculation the vibrational level $v = 32$ of the *B* state lies just above $v = 0$ of the *C* state. The highest vibrational level of the *B* state is 46, and it lies above $v = 2$ of the *C* state. Experimentally the rotational constant B_v for each vibrational level of the *C* state is determined, and an abnormal *v* dependency is found for $v \leq 2$. This is consistent with our calculated inter-relation of vibrational levels of two $^2\Sigma_u^+$ states; the radial coupling of vibronic levels causes the change of the rotational constants.

I-E-4 Theoretical Study on Spectroscopic Properties of Positive, Neutral, and Negative Species of BCl_2 and $AlCl_2$

Kyoung K. BAECK *(Kang-Nung Univ. and IMS)* **and Suehiro IWATA**

Accurate and predictive values of the bond lengths, bond angles, dipole moments, vibration frequencies, and IR intensities of positive(X $^1\Sigma_g^+$), neutral(X $^2A_1$), and negative(X $^1A_1$, a $^3B_1$) species of BCl_2 and $AlCl_2$, are calculated by Becke's three parameter density-functional-theory method, B3LYP-DFT, with the augmented correlation consistent triple- and quadruple-zeta (aug-cc-pvtz and aug-cc-pvqz, respectively) basis sets. The coupled-cluster singles, doubles, and noniterative triples method, CCSD(T), with aug-cc-pvtz is also used to augment the B3LYP-DFT results. The ionization energies and electron affinities are also evaluated by the B3LYP-DFT/aug-cc-pv5z method at the B3LYP-DFT/aug-cc-pvqz geometry and the CCSD(T)/aug-cc-PVQZ method at the CCSD(T)/aug-cc-pvtz geometry, as well as by the G1, G2, CBS-4, and CBS-Q methods. It is shown that the negatively charged species, which have never been studied experimentally, are stable both in singlet and triplet spin states. The Franck-Condon factors within the harmonic approximations are calculated for the electron detachment processes of anions, and the simulated photoelectron spectra for singlet and triplet states of BCl_2^- and $AlCl_2^-$ are given.

I-E-5 The Electronic Structures of HCCS and NCS

Yumin LI and Suehiro IWATA

The number of valence electrons of HCCS and NCS are fifteen, and therefore, the similarity of the electronic structures is expected, though the number of atoms is different. The ground and first excited states of both molecules are $^2\Pi$ and the next state is $^2\Sigma^+$. Three of states of NCS are linear, and Renner-Teller splittings of two $^2\Pi$ states are very small. The UHF wavefunction has a large spin contamination, and the multi-reference description is required. The calculated bond lengths with MRCI calculations are 1.166 for NC and 1.634 for CS in the ground state $^2\Pi$, and 1.232 for NC and 1.650 for CS in the first excited state $^2\Pi$. The wavefuctions indicate that the ground state and the first excited state are π radical, and mixture of $(2\pi)^4(3\pi)^3$ and $(2\pi)^3(3\pi)^4$. In terms of valence bond structures they are $\mathrm{N{\equiv}C{-}\overset{\cdot\,\cdot}{\underset{\cdot}{S}}}$ and $\mathrm{\underset{\cdot}{N}{=}C{=}\overset{\cdot\cdot}{S}}$. The second excited state $^2\Sigma^+$ is the σ radical, $(9\sigma)^1(2\pi)^4(3\pi)^4$, and $\mathrm{N{\equiv}C{-}\overset{\cdot\cdot}{S}\cdot}$. These are also true for three states of HCCS. Because HCCS is tetra-atomic molecules and two bending angles, Renner-Teller effects become complex. The potential energy surfaces for two bending angles are created, and the coupling of two bending angles with the dihedral angle is also examined.

I-E-6 The Electronic Structures of HCCN and HCCP

Yumin LI and Suehiro IWATA

HCCN and HCCP are isovalent molecules, and both are of astronomical interest. The geometric and electronic structures of the ground and low-lying excited states are studied with high levels of ab initio MO methods. The differences and similarities of two molecules are discussed. The ground state of both molecules is the triplet state. The HCC angle of the triplet ground state $^3A''$ of HCCN is about 140 degree, and on the other hand, the CCN angle is almost linear, 175 degree in our best estimate. The optimized bond lengths for CC (1.316 Å) and CN (1.223 Å) suggest the allenic backbone, which is contrary to some of the recent theoretical publication, but agrees with the recent experimental work in Saito's laboratory, IMS. The energy difference between the linear and bent configuration is 1.10 eV. At the linear configuration, the lowest singlet state $^1\Delta$ lies above 8900 cm^{-1}, and the state ordering among the triplet states is $A^3\Delta$, $B^3\Sigma^-$, $C^3\Sigma^+$ and $D^3\Pi$; they are accessible from the ground state by near-UV excitations. The character of the ground triplet state $X^3\Sigma^-$ of HCCP is different from that of HCCN. The molecule is linear, and the calculated harmonic frequencies of two bending modes are 296 and 586 with CCSD(T)/cc-pvtz level of approximation.

The calculated bond lengths of CC (1.231 Å) and CP (1.716 Å) and the electronic wavefunction suggest that the C-C bond is close to a triple bond and the molecule has phosphonic structure $\mathrm{H{-}C{\equiv}C{-}\underset{\cdot}{\dot{P}}}$. The lowest singlet state $^1\Delta$ lies above 8460 cm^{-1} from the bottom of the ground state. The state ordering among the low-lying triplet states is $A^3\Sigma^-$, $B^3\Delta$, $C^3\Sigma^+$ and $D^3\Pi$

I-F Application of Ab Initio Molecular Orbital Methods to Experimentally Relevant Systems

I-F-1 Theoretical Studies of Geometric and Electronic Structures of Novel Molecular Anion $CH_3CO_2I^-$

Morihisa SAEKI *(Univ. Tokyo)*, **Lei ZHU, Tatsuya TSUKUDA** *(Univ. Tokyo)*, **Suehiro IWATA and Takashi NAGATA** *(Univ. Tokyo)*

[*Chem. Phys. Lett.* **280**, 348 (1997)]

Geometric and electronic structure of acetyloxy iodide anion $CH_3CO_2I^-$, which is produced in the reactions of $(CO_2)_N^-$ with CH_3I, are investigated by ab initio MO calculation. It was found that $CH_3CO_2I^-$ is composed as a molecular anion, where acetyloxyl framework binds the I atom through an O-I bond to share the excess electron. The excess electron in the ground state (1^2A') is accommodated into an anti-bonding orbital formed between the $CH_3CO_2^-$ and I. The electron configuration of $CH_3CO_2I^-$ is $\cdots(13a')^2(14a')^2(3a'')^2(15a')^2(4a'')^2(16a')^1$. Based on a simple MO correlation diagram, these orbitals are classified. Interaction of MOs between $CH_3CO_2^-$ and I leads to formation of bonding and antibonding orbitals, which correspond to the 13a' and 16a'. The electronic distribution of 14a' and 3a" orbitals is localized on $CH_3CO_2^-$, while that of 15a' and 4a" is localized on I. On the basis of vertical detachment energies (VDEs) evaluated, two peaks in photoelectron spectrum are attributed to electron detachment from the 16a' and 4a" orbitals. On the other hand, based on the excitation energy and transition dipole moments calculated by MR-CI method, two absorption bands of $CH_3CO_2I^-$ are assigned to electronic transitions of $3^2A' \leftarrow 1^2A'$ and $4^2A' \leftarrow 1^2A'$. These correspond to electronic excitation of 14a' → 16a' and 13a' → 16a'. Photodissociation of $CH_3CO_2I^-$ showed production of $CH_3CO_2^-$ and I, whose branching fraction depends on excitation energy. State correlation diagram of $CH_3CO_2I^-$ indicates crossing of two potential curves, which leads to avoided crossing. The avoided crossing of potential curves results in the energy dependence of branching ratio.

I-F-2 Theoretical Studies of Internal Methyl Rotations in *m*-Xylene: Comparison of Franck-Condon Factors with the Experimental Spectra

Tadayoshi SUZUKI *(Grad. Univ. for Advanced Studies and IMS)*, **Tsutomu IKEGAMI, Masaaki FUJII and Suehiro IWATA**

[*J. Molec. Struct. (THEOCHEM)* in press (1999)]

The potential energy surfaces of internal rotations of two methyl groups were calculated with *ab initio* MO method for the *m*-xylene (1,3-dimethylbenzene) in the ground (S_0), first excited (S_1), and cation ground (D_0) states. The internal rotation levels and their wavefunctions on the theoretically calculated potential energy surfaces were obtained by solving Schrödinger equation for double methyl rotors. The Franck-Condon factors for $D_0 \leftarrow S_1$, and $S_1 \leftarrow S_0$ transitions were calculated and compared with the experimental spectra. A good agreement was obtained not only in level spacings but also in relative intensities in the spectra. The interaction between two methyl rotors was also found to be small, and the rotational levels can be labeled by the irreducible representation of the direct product $G_6 \times G_6$ group.

I-F-3 Theoretical Studies of Internal Methyl Rotations in *o*-Xylene: Coupled Internal Rotation

Tadayoshi SUZUKI *(Grad. Univ. for Advanced Studies and IMS)*, **Tsutomu IKEGAMI, and Suehiro IWATA**

The potential energy surfaces of internal rotations of two methyl groups in *o*-xylene (1,2-dimethylbenzene) are calculated with ab initio MO method for the ground (S_0), first excited (S_1), and cation ground (D_0) states. The internal rotation levels and their wavefunctions on the potential energy surfaces are obtained by solving Schrodinger equation for double methyl rotors. As is expected, the interaction between two methyl rotors is very strong in all states, and the internal rotation levels have to be labeled by the irreducible representation of G_{36} group. A single transition with no change of quantum numbers of the internal rotation dominates the calculated Franck-Condon factors for $D_0 \leftarrow S_1$, and $S_1 \leftarrow S_0$ transitions. Nevertheless, theoretical calculations suggest that weak side bands could reveal the correlated motion of two methyl groups, if they would be ever observed.

I-F-4 Reaction of $OCrO^+$ with a H_2 Molecule

Andreas FIEDLER, Detlef SCHRöDER *(Tech. Univ. Berlin)* **and Suehiro IWATA**

In a tight collaboration with the mass spectrometry group in Berlin the mechanism of the reaction of the chromium dioxide cation with a molecular hydrogen was theoretically examined. We used the B3LYP method to locate possible intermediates and the corresponding transition structures. The resulting qualitative picture for the characteristic critical points on the PESs shall than be verified by further experiments. In the gas phase under thermal conditions $OCrO^+$ slowly activates H_2 (and hydrocarbons) to produce CrO^+ and H_2O. The chromium dioxide cation has already been calculated to have a low-spin doublet ground state and a rather high-lying excited quartet state. The B3LYP approach reproduces these high level calculations in good agreement. An encounter complex with H_2 is a doublet ground state. From a chemical point of view, there are four possible routes for the following σ-bond activation. (1) Oxidative insertion of the metal center into the H-H bond to form a high-valent dihydro-dioxo-chrome compound, (2) A [2+2] pathway, i.e. H-H σ-bond methateses along one Cr-O unit, to generate a oxo-hydro-hydroxo-chrome species, (3) A [3+2] path via a five memberd ring where both oxygen centers simultaneously abstract a hydrogen atom resulting the dihydroxy-chrome cation, (4) A reductive elimination of Cr to form a complex of molecular oxygen, molecular hydrogen, and the chrome cation, followed by H_2 activation. The last two mechanisms are energetically excluded. Products from [2+2] and [2+3] activation paths are much more stable. Both cationic oxo-hydro-hydroxo-chrome and dihydroxy-chrome are low-lying minima on the doublet PES. In addition, the quartet ground state of dihydroxy-chrome is the global minimum. We did not find a stable quartet oxo-hydro-hydroxo-chrome isomer. However, regarding the bottlenecks for these reactions only the [2+2] transition structure (doublet) is located below the entrance channel whereas the [2+3] TS is not accessible at thermal energies. The quartet states are computed to be much higher in energy. Thus, the only viable reaction is the [2+2] activation path on the doublet PES. This is implicitly leading to the doublet oxo-hydro-hydroxo-chrome cation. However, since the dihydroxy isomer is more stable and has a quartet ground state, rearrangement and/or curve crossing to the quartet surface take place after the initial H-H bond breaking. Furthermore, the final reaction product CrO^+ and H_2O implies a further intermediate, i.e., complex of water and chromium oxide cation. The later isomer also has a low-lying quartet ground state. On the doublet PES both TSs for hydrogen shifts in oxo-hydro-hydroxo-chrome cation are calculated to be at the same energy level. The barrier for rearrangement between both products is lower in energy. All located TSs for the hydrogen shifts on quartet and doublet PESs are lower than the lowest TS for the H_2 activation. Thus, after the initial [2+2] activation of H_2 fast rearrangements can take place, probably accompanied by curve crossing to the high-spin PES.

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

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

I-G-1 Effects of Side-Chain Charges on α-Helix Stability in C-Peptide of Ribonuclease A Studied by Multicanonical Algorithm

Ulrich H. E. HANSMANN and Yuko OKAMOTO

[submitted for publication]

We have performed multicanonical Monte Carlo simulations of C-peptide of ribonuclease A. Three analogues of the peptide with charged and neutral side chains were used to study the role of side-chain charges in the stability of the observed α-helix. Two dielectric functions, distance-dependent and constant, are considered to study the effects of solvent contributions. The results are found to be in accord with the implications of CD and NMR experiments of C-peptide where it was found that this peptide has high α-helix content in aqueous solution and that the removal of the side-chain charge of Glu-9^- enhances helix formation. The lowest-energy conformation obtained by our simulations has an α-helix from Ala-4 to Gln-11 in complete agreement with the corresponding structure deduced from an X-ray crystallography experiment of ribonuclease A. The salt bridge between the side chains of Glu-2^- and Arg-10^+, which is known to exist from both NMR and X-ray experiments, is formed only when the side chains are properly charged. Its formation is greatly enhanced when the solvation effects are taken into account.

I-G-2 Stochastic Dynamics Simulations in a New Generalized Ensemble

Ulrich H. E. HANSMANN and Yuko OKAMOTO

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

We develop a formulation for molecular dynamics, Langevin, and hybrid Monte Carlo algorithms in the recently proposed generalized ensemble that is based on a physically motivated realisation of Tsallis weights.

The effectiveness of the methods are tested with an energy function for a protein system. Simulations in this generalized ensemble by the three methods are performed for a penta peptide, Met-enkephalin. For each algorithm, it is shown that from only one simulation run one can not only find the global-minimum-energy conformation but also obtain probability distributions in canonical ensemble at any temperature, which allows the calculation of any thermodynamic quantity as a function of temperature.

I-G-3 The Folding Funnel Landscape for the Peptide Met-Enkephalin

Ulrich H. E. HANSMANN, Yuko OKAMOTO and José N. ONUCHIC *(Univ. Calif. San Diego, U.S.A.)*

[*Proteins* in press]

We study the free energy landscape of the small peptide Met-enkephalin.

Our data were obtained from a *generalized-ensemble* Monte Carlo simulation taking the interactions among all atoms into account.

We show that the free energy landscape resembles that of a funnel, indicating that this peptide is a good folder. Our work demonstrates that the energy landscape picture and folding concept, developed in the context of simplified protein models, can also be used to describe the folding in more realistic models.

I-G-4 Finite-Size Scaling of Helix-Coil Transitions in Poly-Alanine Studied by Multicanonical Simulations

Ulrich H. E. HANSMANN and Yuko OKAMOTO

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

We report results from multicanonical simulations of poly-alanine.

Homopolymers of up to 30 amino acids were considered and various thermodynamic quantities as a function of temperature calculated. We study the nature of the observed helix-coil transition and present estimates for critical exponents.

I-G-5 Singular Behavior of the RISM Theory Observed for Peptide in Salt Solution

Masahiro KINOSHITA *(Kyoto Univ.)*, **Yuko OKAMOTO and Fumio HIRATA**

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

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

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

I-G-6 Analysis on Conformational Stability of C-Peptide of Ribonuclease A in Water Using the Reference Interaction Site Model Theory and Monte Carlo Simulated Annealing

Masahiro KINOSHITA *(Kyoto Univ.)*, **Yuko OKAMOTO and Fumio HIRATA**

[submitted for publication]

Solvation structure and conformational stability of the C-peptide fragment of ribonuclease A in pure water have been analyzed using the full reference interaction site model (RISM) theory. The charged groups in the side chains of Lys-1^+, Glu-2^-, Lys-7^+, Arg-10^+, and His-12^+ (in particular, the four like-charged groups) play substantial roles in stabilizing the conformations. The solvation free energy and the conformational energy are governed by the contribution from the electrostatic interaction with water and the intramolecular Coulombic energy, respectively, and the conformational stability is determined by competition of these two factors.

The contribution from the hydrophobic hydration and the van der Waals and torsion terms in the conformational energy are less important, which is in contrast with the result for Met-enkephalin. The Monte Carlo simulated annealing combined with the RISM theory has been applied to the C-peptide using an almost fully extended conformation as the initial one. The conformation first changes in the direction that the charged groups in the side chains are more exposed to water, and in particular, the positively charged groups are closer together. Thus, the solvation free energy decreases greatly in the initial stage. Although this leads to significant increase in the intramolecular Coulombic repulsion energy, the decrease in the solvation free energy dominates. In the later stage, however, further decrease in the solvation free energy gives rise to even larger increase in the intramolecular Coulombic repulsion energy, and the conformational change is greatly decelerated. The conformations thus stabilized in four different runs of the combined program are quite similar. The peptide conformation in water is stabilized far more rapidly than in gas phase.

I-G-7 β-Sheet Formation in BPTI(16-36) by Monte Carlo Simulated Annealing

Yuko OKAMOTO, Masato MASUYA, Miho NABESHIMA *(Nara Women's Univ.)* **and Takashi NAKAZAWA** *(Nara Women's Univ.)*

[submitted for publication]

Performing Monte Carlo simulated annealing simulations from randomly chosen intial conformations, we have obtained a β-sheet structure as the lowest-energy conformation. The solvent effects were included by the term that is proportional to the solvent-accessible surface area. This lowest-energy structure has a type II' β-turn and three characteristic intrachain hydrogen bonds that connect the two β-strands. It turns out that the positions of these β-turn and hydrogen bonds are in remarkable agreement with the implications of an NMR experiment of the same fragment.

I-H Theoretical Studies of Chemical Reaction Dynamics

I-H-1 Cumulative Reaction Probability without Absorbing Potentials

Oleg I. TOLSTIKHIN *(Lebedev Physical Inst. and IMS)*, **Valentin N. OSTROVSKY** *(Univ. St. Petersburg and IMS)* **and Hiroki NAKAMURA**

[*Phys. Rev. Lett.* **80**, 41 (1998)]

Cumulative reaction probability, introduced in the collision theory by W. H. Miller [*J. Chem. Phys.* **62**, 1899 (1975)], characterizes a net efficiency of a rearrangement process as a function of the total energy of the collision system. We derive a formula that expresses this quantity in terms of the outgoing wave Green function. Our formula is free from the ambiguities of previous formulations; in particular, no absorbing potentials are required for its implementation. The formula has a potentially wide range of applications in atomic and molecular collision physics. As an illustration, we consider the rearrangement processes in the $dt\mu$ system for the energies up to the $n = 6$ threshold.

I-H-2 Hyperspherical Elliptic Coordinates for the Theory of Light Atom Transfer Reactions in Atom-Diatom Collisions

Oleg I. TOLSTIKHIN *(Lebedev Physical Inst. and IMS)* **and Hiroki NAKAMURA**

[*J. Chem. Phys.* **108**, 8892 (1998)]

We formulate and demonstrate a new method for quantum 3D calculations of light atom transfer reactions in atom-diatom collisions. The method follows a general scheme of the hyperspherical method, in common with other hyperspherical formulations in the field. The main novelty consists in the hyperspherical elliptic coordinates (ξ,η) used to parametrize the hypersphere. These coordinates have been introduced recently for studying three-body Coulomb systems, and here we apply them to study a system of three atoms. The coordinates are defined and their relation with the Smith-Whitten and Delves coordinates is explored. On account of a big difference between vibrational and rotational excitation energies in molecules, the hyperspherical adiabatic Hamiltonian allows adiabatic separation between ξ and η. This not only greatly facilitates solution of the hyperspherical adiabatic eigenvalue problem, but also provides an approximate classification of the states by a pair of indices (n_ξ, n_η) representing vibrational and rotational quantum numbers simultaneously for a reagent and product. Another novel technology exploited here is the Slow/Smooth Variable Discretization (SVD) method. The SVD is used for treating nonadiabatic couplings between the ξ and η motions, as well as between the motions with respect to the hyperradius and the hyperangular variables. The whole scheme is illustrated by calculations for the reaction $O(^3P)+HCl \rightarrow OH + Cl$ for zero total angular momentum. It is shown to be very efficient, accurate, and providing a framework of choice for elucidating light atom transfer reaction mechanisms.

I-H-3 Quantum Mechanical Elucidation of Reaction Mechanisms of Heavy-Light-Heavy Systems: Role of Potential Ridge

Katsuyuki NOBUSADA, Oleg I. TOLSTIKHIN *(Lebedev Physical Inst. and IMS)* **and Hiroki NAKAMURA**

[*J. Chem. Phys.* **108**, 8992 (1998)]

A new idea to elucidate quantum reaction dynamics of heavy-light-heavy (HLH) systems is proposed on the basis of the hyperspherical elliptic coordinate approach. This coordinate system has a big advantage of nicely expressing good vibrational adiabaticity in the HLH systems. Taking this advantage, the concept of potential ridge is introduced, for the first time, in three-dimensional reactions. The potential ridge is proved to be very useful to extract some important avoided crossings which dominate the reaction dynamics. In fact, qualitative features of the reaction dynamics can be interpreted in terms of non-adiabatic transitions at those important avoided crossings near the potential ridge. Examples are: (i) onset of reaction for specified initial rotational states, and (ii) major reactive transition for a specified initial rotational state. Avoided crossings to the left of the potential ridge are also useful to interpret certain aspects of reactions accompanying vibrational transitions. The new idea mentioned above is applied to a typical HLH reaction $O(^3P)+HCl \rightarrow OH + Cl$ with the use of two types of potential energy surfaces.

I-H-4 Quantum Reaction Dynamics of Cl + HCl → HCl + Cl: Vibrationally Nonadiabatic Reactions

Katsuyuki NOBUSADA, Oleg I. TOLSTIKHIN *(Lebedev Physical Inst. and IMS)* **and Hiroki NAKAMURA**

[*J. Mol. Str. (THEOCHEM)* in press]

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

I-H-5 Semiclassical Treatment of Resonances in the Collinear O + HO Exchange Reaction

Gennady V. MIL'NIKOV *(Inst. Structual Macro - kinetics, Russia and IMS)*, **Chaoyuan ZHU, Hiroki NAKAMURA and Vladimir I. OSHEROV** *(Inst. Chem. Phys., Russia and IMS)*

[*Chem. Phys. Lett.* **293**, 448 (1998)]

Feshbach type sharp resonances appearing in the O + HO collinear reaction are analyzed by the newly completed semiclassical theory for the Landau-Zener-Stueckelberg type curve crossings. Not only the resonance positions, but also the widths are nicely reproduced in comparison with the exact numerical calculations, even when the widths are as small as $10^{-8} \sim 10^{-11}$ *a.u.* The semiclassical theory is extended so as to be applicable to the case that the bottom of upper adiabatic potential is higher than the crossing point.

I-H-6 Four Mathematical Dimensional Quantum Mechanical Studies of Tetra-Atom Systems: State-to-State $J = 0$ Probabilities for the H_2 + OH → H_2O + H Reaction

Henrik SZICHMAN *(Soreq NRC, Israel and IMS)*, **Michael BAER** *(Soreq NRC, Israel)* **and Hiroki NAKAMURA**

[*J. Chem. Phys.* **107**, 3521 (1997)]

This paper presents reactive state-to-state $J = 0$ probabilities for the title system as obtained in a four-mathematical-dimensional quantum mechanical treatment. The present treatment differs from our previous one by the fact that in addition to the three Jacobi radial coordinates also the angular coordinate related to the H_2 axis is treated as coordinates. As a result only the Jacobi angle related to the OH axis is treated as a parameter and the final probabilities follow from an integration over this angle (the out-of-plane angle, β, is eliminated by using a β-averaged potential). The calculations yielded final rotational and vibrational distributions that were analyzed and discussed with respect to more accurate (i.e., five- and six-mathematical-dimensional) results.

I-I Theory of Nonadiabatic Transitions

I-I-1 Semiclassical Theory of Multi-Channel Curve Crossing Problems: Nonadiabatic Tunneling Case

Chaoyuan ZHU and Hiroki NAKAMURA

[*J. Chem. Phys.* **107**, 7839 (1997)]

Based on the new two-state theory of curve crossing recently completed by the authors, a compact and powerful theory is formulated for a general resonant multi-channel scattering with nonadiabatic tunneling (NT) type curve crossings. This theory is demonstrated to work remarkably well by comparing with the numerical solutions of close-coupling equations. Even detailed structures of overlapping resonances are nicely reproduced by the theory. Furthermore, this theory is very simple, not requiring any non-unique diabatization procedure, any complex calculus and any information on the couplings, neither diabatic nor nonadiabatic. The theory is based only on the adiabatic potentials on the real axis. Together with the previously proposed theory for the Landau-Zener (LZ) type curve crossings, the present semiclassical theory provides a complete picture of and a very powerful tool for multi-channel curve crossing problems.

I-I-2 Semiclassical Theory of Nonadiabatic Transition in a Two-State Exponential Model

Vladimir I. OSHEROV *(Inst. Chem. Phys., Russia and IMS)*, **Vladimir G. USHAKOV** *(Inst. Chem. Phys., Russia)* **and Hiroki NAKAMURA**

[*Phys. Rev. A* **57**, 2672 (1998)]

A general two-state exponential potential model is solved with use of the Bessel transformation and the WKB (Wentzel-Kramers-Brillouin) type semiclassical approximation. Accurate expressions are obtained for the nonadiabatic transition probability for one passage of the transition point and for the two dynamical phases.

Functionalities of these quantities in terms of two basic parameters are the same as those obtained before by Nikitin. The two basic parameters are, however, expressed in more general and accurate forms. Accuracies of these expressions are numerically confirmed.

The three quantities, the nonadiabatic transition probability and the two dynamical phases, constitute the nonadiabatic transition matrix and can be used to describe various (spectroscopic as well as scattering) processes not only for a two-state but also for a multichannel system. A possible generalization of the present theory is also briefly discussed to formulate a unified theory which can cover both Landau-Zener-Stueckelberg and Rosen-Zener-Demkov cases within the adiabatic state representation.

I-I-3 Improvement of the Adiabatic Phase

Integral for the Landau-Zener-Type Curve Crossing

Chaoyuan ZHU and Hiroki NAKAMURA

[*J. Chem. Phys.* **109**, 4689 (1998)]

We have established the new semiclassical theory for the two-state Landau-Zener-Stueckelberg-type curve crossing problems and have demonstrated their usefulness for various multichannel curve crossing problems in both time-independent and time-dependent cases. For both Landau-Zener (LZ) and nonadiabatic-tunneling (NT)-type transitions, our new theory can be solely based on the adiabatic potentials on the real axis and is free from searching complex crossing points and evaluating complex phase integrals. As a result, the theory can handle multichannel problems basically without any restriction to the number of crossings and channels involved. We have realized, however, that the theory in NT-type works much better than that for the LZ-type, and found that this is due to the adiabatic phase in the very strong diabatic coupling regime. In this note we report its improvement. This is quite important, because it is practically almost impossible to find complex crossing points among multichannel adiabatic potentials.

I-I-4 Patterns of Time-Propagation on the Grid of Potential Curves

Valentin N. OSTROVSKY *(Univ. St. Petersburg, Russia and IMS)* **and Hiroki NAKAMURA**

[*Phys. Rev. A* in press]

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

I-J New Way of Controlling Molecular Nonadiabatic Processes

I-J-1 Control of Time-Dependent Nonadiabatic Processes by an External Field

Yoshiaki TERANISHI *(Grad. Univ. Adv. Stud.)* **and Hiroki NAKAMURA**

[*Phys. Rev. Lett.* **81**, 2032 (1998)]

A new idea of controlling nonadiabatic transitions by an external field is proposed. The basic principle is to periodically sweep an external field at each level crossing to make the overall transition probability from an initial state to any desirable final state equal to unity. The recently completed semiclassical theory of nonadiabatic transition enables us to analytically deal with this problem. The present idea may be applicable to various physical and chemical problems, whenever level crossings are created by an extern field.

I-J-2 New Way of Controlling Molecular Processes by a Time-Dependent External Field

Yoshiaki TERANISHI *(Grad. Univ. Adv. Stud.)* **and Hiroki NAKAMURA**

A new way of controlling molecular processes by using a time-dependent external field is proposed. As was discussed in the previous paper, the basic idea is to completely control nonadiabatic transitions at avoided crossings of potential curves by periodically sweeping the external field. The control conditions can be formulated analytically. The external field can be anything like magnetic, electric, or laser field. In the case of laser field, one can use both frequency and intensity as control parameters. Various semiclassical theories of nonadiabatic transitions can be nicely utilized to formulate the problem. As an example, a one-dimensional model of ring puckering isomerization of trimethyleneamine is discussed.

I-K Theoretical Studies of Characteristics and Dynamics of Superexcited States of Molecules

I-K-1 Characteristics and Dynamics of Superexcited States of Diatomic Molecules: General Theoretical Procedure

Miyabi HIYAMA *(Grad. Univ. Adv. Stud.)*, **Nobuhiro KOSUGI and Hiroki NAKAMURA**

[*J. Chem. Phys.* **107**, 9370 (1997)]

A general theoretical procedure to analyze the characteristics and dynamics of superexcited states of diatomic molecules is developed. It utilizes the following three methods effectively: (1) quantum chemical methods to evaluate basic parameters of the superexcited states, (2) spectroscopic experiments to improve the basic information obtained theoretically, and (3) multi-channel quantum defect theory (MQDT) to analyze couplings among various kinds of states and to clarify the dynamics. This procedure is composed of seven steps, including a method to evaluate the electronic coupling of the first king of superexcited state to ionization continuum which is newly proposed here. The two-center Coulomb function in the field of the corresponding diatomic molecular ion is used to evaluate this coupling. This can be done by incorporating the Coulomb functions into an ab initio quantum chemical code. The whole procedure is illustrated for the CO molecule.

I-K-2 Analytical Treatment of Singular Equations in Dissociative Recombination

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The Lippmann-Schwinger type singular integral equation, which arises in the multichannel quantum defect theory (MQDT) approach to the dissociative recombination process, is investigated. The singularity is treated analytically by introducing an energy dependent quadrature. In many cases of physical interest the energy kernel of the equation is well approximated to be separable and an analytical solution becomes possible. The solution is illustrated by taking the case of H_2^+ as an example, and is shown to be better than the other available methods such as the perturbation and the grid methods.

I-K-3 Electron Attachment and Vibrational Excitation in Hydrogen Iodide: Calculations Based on the Nonlocal Resonance Model

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[*Z. Phys. D* **42**, 181 (1997)]

The nonlocal resonance model developed earlier for the description of the collision of low-energy electrons with HCl and HBr has been adapted to the electron-HI collision system. The parameters of the model have been determined by fitting experimental high-resolution data for the attachment cross section in HI in the energy range 0-170 meV. Moreover, ab initio electronic-structure data for the electronic ground-state potential-energy function of HI^- have been taken into account. Within the resulting model, cross sections for vibrational excitation and dissociative attachment processes in HI and DI have been calculated over a reasonably wide energy range. No high-resolution experimental data are available for comparison.

I-L Siegert Pseude-State Formulation of Scattering Theory

I-L-1 Siegert Pseude-State Formulation of Scattering Theory: One-Channel Case

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[*Phys. Rev. A* **58**, 2077 (1998)]

Siegert pseude-states (SPS) are defined as a finite basis representation of the outgoing wave solutions to radial Schroedinger equation for cutoff potential, and the problem of their calculation is reduced to standard linear algebra easily implementable on computers. For a sufficiently large basis and the cutoff radius, the set of SPS includes bound, weakly antibound, and narrow complex-energy resonance states of the system, i.e. all the physically meaningful states observable individually. Moreover, the set is shown to posess certain orthogonality and completeness properties which qualify it as a discrete basis suitable for expanding the continuum. We rederive many results of the theory of Siegert states in terms of SPS and obtain some new relations not known previously. This not only makes the results for the first time practically applicable, but also sheds a new light on their mathematical nature. In particular, we show how the Mittag-Leffler expansion for the outgoing wave Green function and the scattering matrix can be obtained on the basis of very simple algebraic relations, without assuming them to be meromorphic functions. Explicit construction of these two fundamental objects completes the SPS formulation of scattering theory for one-channel case. The computational efficiency of this approach is illustrated by a number of numerical examples.

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

I-M-1 Fifth-Order Two-Dimensional Vibrational Spectroscopy of a Morse Potential System in Condensed Phases

Yoshitaka TANIMURA

[*Chem. Phys.* **233**, 217 (1998)]

The nonlinear optical response of a molecular system in the condensed phase subjected to a series of five off-resonant femtosecond laser pulses has been studied using a quantum Fokker-Planck equation. The third- and fifth-order response functions, which are equivalent to the second- and third-order correlation functions of the molecular coordinate were obtained form the equation of motion. Assuming the potential surface of a Cesium dimer [Cs_2], which is modeled by a Morse potential, and considering both the linear and nonlinear coordinate dependence of the polarizability, we calculated the third- and fifth-order response functions for various temperatures and heat-bath couplings. The temporally two-dimensional (2D) profiles of the fifth-order signal effects both the shape of potential and the coordinate dependence of the polarizability, even at strong damping. The non-linearities caused by the anharmonic potential and by the nonlinear polarizability have different temperature dependence. This indicates that fifth-order two-dimensional spectroscopy carried out for a different temperature allows us to access information of the potential and the polarizability.

I-M-2 Pump-Probe Spectra and Nuclear Dynamics for a Dissipative Molecular System in a Strong Laser Field: Predissociation Dynamics

Yutaka MARUYAMA *(Grad. Univ. Adv. Stud.)* **and Yoshitaka TANIMURA**

[*Chem. Phys. Lett.* **292**, 28 (1998)]

The predissociation dynamics of a molecular system under a strong laser field in the condensed phase is investigated by direct numerical integration of the multi-state quantum Fokker-Planck equation. Numerical calculations of probe absorption spectra driven by a strong pump pulse are presented, and discussed. The results show dynamical Stark splitting, but, in contrast to the Bloch equations which contain an infinite-temperature dephasing, we find that at finite temperatures their peaks have different heights even when the pump pulse is on resonance. Furthermore we observe the effect of the diabatic coupling between excited and dissociative states as the peaks on the spectra.

I-M-3 Coherent Two-Dimensional Raman Scattering: Frequency-Domain Measurement of the Intra- and Intermolecular Vibrational Interactions

Minhaeng CHO *(IMS and Korea Univ.)* **Ko OKUMURA and Yoshitaka TANIMURA**

[*J. Chem. Phys.* **108**, 1326 (1998)]

A new experiment of frequency-domain coherent two-dimensional Raman scattering is theoretically proposed. By using three fields whose wave vectors and frequencies are independently controlled, one can measure the nonlinear Raman responses in either gas or condensed phases. The connection to the time-domain femtosecond two-dimensional Raman spectroscopy is completely established. By considering several limiting cases in detail, it is found that from the coherent 2D Raman scattering spectrum one can obtain quantitative information on the anharmonicity, anharmonic mode coupling, and polarizability coupling.

I-M-4 Sensitivity of Two-Dimensional Fifth-Order Raman Response to the Mechanism of Vibrational Mode-Mode Coupling in Liquid Molecules

Ko OKUMURA and Yoshitaka TANIMURA

[*Chem. Phys. Lett.* **278**, 175 (1997)]

We study coupling mechanism of inter- and intramolecular modes of liquids by using a multi-mode Brownian oscillators model. The coupling between modes comes into play through polarizability and/or potential expanded with respect to vibrational coordinates. We take into account these two causes of coupling and present analytical expressions for the Fourier transform of the time-domain fifth-order Raman signal. We demonstrate a notable sensitivity of the Fourier-transformed quantity to the coupling mechanism through numerical calculations for chloroform.

I-M-5 Two-Dimensional THz Spectroscopy of Liquids: Nonlinear Vibrational Response to a Series of THz Laser Pulses

Ko OKUMURA and Yoshitaka TANIMURA

[*Chem. Phys. Lett.* **295**, 298 (1998)]

We propose a nonlinear experiment utilizing the nonlinear interaction with THz pulses, whose generation has recently become well established. In the lowest nonlinear process, we have two controllable delay times. This is another optical analogue of the two-dimensional (2D) NMR as the recently developed 2D Raman spectroscopy. Our model calculation for liquid water demonstrates the striking capability of the proposed technique, clearly distinguishing two types of anharmonicity in the low-frequency modes.

I-M-6 Optimized Perturbation Approach to a Dissipative System: Correlation Functions of Anharmonic Oscillators

Yoko SUZUKI and Yoshitaka TANIMURA

[*Phys. Rev. E* in press]

We apply the optimized perturbation theory (OPT) to study the dynamics of a anharmonic potential system in coupled to a heat bath. The OPT combines the techniques based on the variational principle and the perturbative expansion. The first order approximation of the OPT agrees with the Feynman's variational theory developed for the polaron problem. The OPT makes it possible to deal with anharmonic potential system in non-perturbative way. Combined with inversion method which is the technique to carry out the Legendre transformation, we take effectively into account of the information lacked in the OPT alone, for example the ansymmetry of potential. We then develop a formalism to calculate partition functions and two-time correlation functions of a coordinate which relate to the linear absorption spectrum in laser experiments. We use this procedure so as to study the dynamics of a Morse potential system and a double well potential system coupled to a heat-bath, respectively.

I-N Theoretical Studies of Molecular System Coupled to a Glass Environment

I-N-1 Spectral Random Walks and Line Broadening of Impurity Molecules in an Ising Spin Glass Environment

Yoshitaka TANIMURA, Hiroshi TAKANO *(Keio Univ.)* **and Joseph KLAFTER** *(Tel-Aviv Univ.)*

[*J. Chem. Phys.* **108**, 1851 (1998)]

Transition energy fluctuations in impurity molecules, embedded in an inhomogeneous environment, are investigated within an Ising spin model of the environment. The spatially distributed impurity molecules are assumed to interact with the Ising spin glass through dipole-dipole type of interaction. We calculate the fluctuations in the transition energies of impurity molecules, for different temperatures and various Ising parameters, and find that the spectral distribution of the fluctuations follows approximately a 1/f power law. The fluorescence spectra of the impurity molecules yield microscopic information about domain structures in the Ising environment. In the case of large disorder, the distribution of transition energies shows profiles similar to those observed in single molecule spectroscopy.

I-N-2 Absorption Line Shape of Impurity Molecule Driven by a Fractal Noise

Gautam GANGOPADHYAY and Yoshitaka TANIMURA

[*Chem. Phys. Lett.* **289**, 97 (1998)]

We have applied the quantum master equation to simulate a two-level system driven by a fractal noise in a dissipative environment. The fractal noise is assumed to be a two-state process with $\pm\Delta$ and characterized by its correlation function $1/\tau^{\beta}$ where $0 < \beta < 1$. Steady state absorption spectrum for the system is obtained analytically for a monochromatic laser excitation. A dramatic blue shift as well as a broadening of the absorption peak, due to the interference between the fractal noise and the natural damping, is observed.

I-O Ab Initio Molecular Orbital studies of Organic Conductors

I-O-1 Ab Initio MO Studies on Electronic States of DCNQI Molecules

Yutaka IMAMURA *(Grad. Univ. Adv. Stud.)*, **Seiichiro TEN-NO and Yoshitaka TANIMURA**

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

I-O-2 Theoretical Study on Electron Correlation of 1-D (DCNQI)2M (M = Li, Ag) Salts

Yutaka IMAMURA *(Grad. Univ. Adv. Stud.)*, **Seiichiro TEN-NO, Kenji YONEMITSU and Yoshitaka TANIMURA**

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

We study electronic states of the (DCNQI)2M (M = Li and Ag) salts based on the ful configuration interaction (FCI) method using effective Hamiltonians derived from the ab initio molecular orbital theory. FCI results of the DCNQI tetramer and octamer models indicate that the ground state has the antiferromagnetic and charge ordering correlations. It corresponds to the 2 kF spin density wave and 4 kF charge density wave states (SDW and CDW). In the octamer model, it is also found that some low-lying excited states have similar spin-flipped CDW correlations and the antiferromagnetic correlation is weakened.

I-P Electron and Positron Scattering from Polyatomic Molecules

The interaction potential between the positron or electron and a molecule consists of three components: electrostatic, exchange and polarization. The static potential arises from the interaction between the projectile and the electrostatic field of the molecule. Thus the static potential for the positron collision is the same as that for the electron collision except for its sign. There is no exchange interaction in the case of positron-molecule collision. In the asymptotic (long-range) region, the polarization interaction for the positron-molecule collision is exactly the same as that for the electron-molecule collision. As the projectile comes closer to the molecule, the distortion of the molecular charge cloud becomes different for different projectiles. The polarization potential at short to intermediate range, particularly its anisotropic part, should be different for the two projectiles. The polarization interaction is another example of long-range interaction, but the cumulative effects of the two types of interactions are totally different for the two projectiles (additive for one and canceling for another).

Due to the complexity of the potential, an electron is known to be temporarily captured by a molecule. This gives rise to a so called "shape resonance" in the electron scattering from a molecule. It is of much interest to see if a similar resonance can occur in the positron scattering from a molecule. The shape resonance affects also the rotational and vibrational excitation processes. Even if no shape resonance occurs, the dependence on the projectile (i.e., positron vs. electron) can appear differently in the processes of rotational and vibrational excitations. A comparative study of the positron- and electron-molecule collisions, particularly that of the rotational and vibrational excitation (and dissociation), would be fruitful in understanding the dynamics of the interaction of both the positron and electron with molecules. In this respect, collisions involving polyatomic molecules are of much interest.

I-P-1 A Comparative Study of Electron- and Positron-Polyatomic Molecule Scattering

Mineo KIMURA *(Yamaguchi Univ. and IMS)*, **Osamu SUEOKA and Akira HAMADA** *(Yamaguchi Univ.)* **and Yukikazu ITIKAWA** *(ISAS)*

The present article is concerned with polyatomic molecules than with diatomic and triatomic ones, which were mainly treated in the earlier review article by Kauppila and Stein.1) We discuss a few new and intriguing features observed for the first time recently for positron scattering from large polyatomic molecules, and provide with an analysis from combined theoretical and experimental points of view.

All possible processes by electron and positron impacts are listed in Table 1. For electron impact, a few data are available for total, elastic, momentum transfer, rovibrational excitation, and some electronic excitation and ionization processes, while for positron impact, very limited information for total cross section for limited species of atoms and molecules and virtually no data exists for inelastic processes. From a comparative study between electron and positron impact, we can shed a light on basic schemes of interaction and scattering dynamics, and hence provide the understanding of basic physics at much deeper level.

Reference

1)W. E. Kauppila and T. E. Stein, *Adv. At. Mol. Opt. Phys.* **26**, 1 (1989).

Table 1. Processes possible for electron and positron scattering.

e_p + AB(v,J)	→	e_p + AB	elastic
	→	$e_p + e^- + AB^+$	ionization
	→	e_p + AB*	electronic excitation
	→	e_p + AB(v', J')	rovibrational excitation
	→	AB^-	electron attachment
	→	AB^+	positron attachment (not observed yet)
	→	$(e^+e^-) + AB^+$	positronium formation (Positron only)
	→	$h\nu + AB^+$	direct annihiration (Positron only)

I-P-2 Mode-Dependence in Vibrational Excitation of CO_2 Molecule by Electron and Positron Impacts

Mineo KIMURA *(Yamaguchi Univ. and IMS)*, **Michiya TAKEKAWA** *(ISAS)*, **Yukikazu ITIKAWA** *(ISAS)*, **Hideki TAKAKI and Osamu SUEOKA** *(Yamaguchi Univ.)*

We have found theoretically, for the first time, that vibrational excitations of CO_2 molecule by electron (e^-) and positron (e^+) impacts are strongly dependent on the charge of the projectile at impact energy below 6 eV. For the symmetric-stretching mode, the excitation cross section of e^- impact is larger by two-to-three orders of magnitude than that of e^+ impact, while for bending and asymmetric-stretching modes, the magnitude of both cross sections for e^- and e^+ impacts are nearly comparable. These results are qualitatively confirmed experimentally, and are interpreted as the difference of interactions and incident-e^- or -e^+ wavefunctions.

I-P-3 Total Cross Sections of Electron and Positron Collisions with C_3F_8 and C_3H_8 Molecules, and Differential Elastic and Vibrational Excitation Cross Sections by Electron Impact on These Molecules

Hiroshi TANAKA, Yoshio TACHIBANA, Masashi KITAJIMA *(Sophia Univ.)*, **Osamu SUEOKA, Hideki TAKAKI, Akira HAMADA** *(Yamaguchi Univ.)* **and Mineo KIMURA** *(Yamaguchi Univ. and IMS)*

Total cross section for electron (e^-) and positron (e^+) scattering from C_3H_8 and C_3F_8 have been measured from 0.8 to 600 eV and 0.7 to 600 eV, respectively. We have also investigated differential elastic cross sections DCS's by electron impact from 2.0 eV to 200 eV, which are compared with the present theoretical result. For e^- scattering from C_3H_8, the cross sections are found to be larger by a factor of two than these of e^+ scattering below 20-30 eV measured and they show a large peak at 8 eV due to a shape resonance, in addition to a shoulder-like structure in the region of 20 - 40 eV. For e^- scattering from C_3F_8, the cross sections are again larger by at least a factor of two than those of e^+ scattering below 50 eV, and have two peaks at 4 and 8 eV, followed by a broad peak in the region of 20 - 40 eV. Some small structures overlies on the broad hump. Both cross sections of e^- and e^+ impacts for C_3H_8 and C_3F_8 quickly approach to each other beyond 200 eV. From DCS's study, we have been able to provide with more detailed information of shape resonances, and also have carried out some analysis of resonances in vibrational excitation results. In general, the total and integrated elastic cross sections are in good qualitative and quantitative agreement.

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 refereed to as RISM-SCF based on the integral equation theory of molecular liquids (RISM) and the ab initio electronic structure theory (SCF).1) The integral equation approach replaces the reaction field in the continuum models by a microscopic expression in terms of the site-site radial distribution functions between solute and solvent.

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

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

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

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

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

The same Fock operator can be derived from a variational principle.2) Defining the Helmholtz free energy A as follows, 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 Molecular Theory of Solvent Effect on keto-enol Tautomers of Formamide in Aprotic Solvents: RISM-SCF Approach

Tateki ISHIDA *(Kyoto Univ.)*, **Fumio HIRATA, Hirofumi SATO and Shigeki KATO** *(Kyoto Univ.)*

[*J. Phys. Chem. B* **102**, 2045 (1998)]

By using RISM-SCF method, the optimized geometries and solvation free energies of the keto and enol tautomers of formamide were calculated in six organic aprotic solvents (CS_2, CCl_4, DME, THF, acetonitrile, and DMSO). From the analysis of the solvation free energies, it was shown that the solute-solvent hydrogen bonding largely contributed to them and that the ability of the solvent to form hydrogen bondings is very important. It was also shown that Taft's b parameters are well-correlated to the calculated well-depth of hydrogen bonding. The results that the solvation free energies for both the tautomers showed the irregularity in acetonitrile solution are in qualitative accord with the empirically determined solvent parameters. The empirical measure of solvent ability to form hydrogen-bonding with solute is explained at a molecular level.

The solvent effects on the energy difference between the keto-enol tautomers were examined. It was found that the keto tautomer was stabilized largely compared to enol form. These tendencies are consistent with the experimental and previous theoretical results. In both tautomers, the dipole moments of solutes were enhanced in polar solvents and the geometric structures were changed, so as to increase the solute dipole moment. It was found that the tendency of solute dipole moments was correlated to Taft's parameters with respect to solvent polarity.

I-Q-2 Theoretical Study of the Solvent Effect on Triiodie Ion in Solutions

Hirofumi SATO, Fumio HIRATA and Anne B. MYERS *(Univ. Rochester)*

[*J. Phys. Chem. A* **102**, 2065 (1998)]

The free energy surfaces of I_3^- in aqueous, methanol and acetonitrile solutions as well as in the gas phase are examined in both ground and excited states by means of the *ab initio* RISM-MCSCF (reference interaction site model — multiconfigurational self consistent field) method. The $X^1\sum_g^+$ state in the gas phase has a highly symmetrical $D_{\infty h}$ geometry as its stable structure. In solution phases, the electronic structure of I_3^- is strongly affected by the surrounding solvent molecules and the energy profiles are drastically changed. Especially in aqueous solution, the ground-state free-energy surface around the gas phase equilibrium geometry becomes virtually flat, indicating an increased population of asymmetrical structure due to the solvent effect. It is suggested that this broken symmetry can explain the appearance of transitions in the IR and Raman spectra which are symmetry forbidden in the gas phase.

I-Q-3 Theoretical Study for Autoionization of Liquid Water: Temperature Dependence of the Ionic Product (pK_W)

Hirofumi SATO and Fumio HIRATA

[*J. Phys. Chem. A* **102**, 2603 (1998)]

The temperature dependence of the ionic product of water (pK_w) is investigated theoretically by means of ab initio electronic structure theory combined with the extended reference interaction site method in statistical mechanics of molecular liquids (RISM-SCF/MCSCF method). The chemical equilibrium $H_2O + H_2O = H_3O^+ + OH^-$ is studied, in which water molecules, hydronium ions, and hydroxide ions are regarded as "solute" molecules in aqueous solution. Molecular geometries, electronic structures, pair correlation functions, and free energy components of those species as well as their temperature dependence are calculated. It is shown that the hydroxide anion is polarized more easily by surrounding solvent compared to the other species. The solvent-induced electronic structure relaxes toward that in the gas phase as temperature increases. The hydroxide anion exhibits the largest temperature dependence in the electronic structure as well as in solvation structure. It is found that changes in the solvation free energies drive the chemical equilibrium toward the left-hand side (association) as temperature increases, while energies associated with solvent-induced reorganization of electronic structure make the opposite contribution. The temperature dependence of pK_w is dominated by the latter contribution, which gives rise to good agreement with the experimental results. It is suggested that the observed temperature dependence of pK_w is related to the great sensitivity of the electronic structure of OH^- on the solvent effect.

I-Q-4 The Syn-/Anti- Conformational Equilibrium of Acetic Acid in Water Studied by the RISM - SCF/ MCSCF Method

Hirofumi SATO and Fumio HIRATA

[*J. Mol. Struct.(theochem)* in press]

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

I-Q-5 RISM-SCF Study for the Free Energy Profile of Menshutkin Type Reaction $NH_3 + CH_3Cl \rightarrow NH_3^+CH_3 + Cl^-$ in Aqueous Solution

Kazunari NAKA *(Kyoto Univ.)*, **Hirofumi SATO, Akihiro MORITA** *(Kyoto Univ.)*, **Fumio HIRATA and Shigeki KATO** *(Kyoto Univ.)*

[submitted]

The free energy profile for the Menshutkin type reaction $NH_3 + CH_3Cl \rightarrow NH_3^+CH_3 + Cl^-$ in aqueous solution is studied using the RISM-SCF method. The effect of electron correlation on the free energy profile is estimated by the RISM-MP2 method at the HF optimized geometries along the reaction coordinate. The vibrational frequencies at the reactant, transition state and product are found to undergo a large influence by the solvation and these are utilized to calculate the zero-point energy correction of the free energy profile. The computed barrier height and reaction exothermicity are in reasonably agreement with those of the experiment and the previous calculations. The change of solvation structure along the reaction path are represented by the radial distribution functions between the solute-solvent atomic sites. The mechanisms of the reaction are discussed from the view points of solute electronic and solvation structures.

I-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 confomational stability of biomolecules in terms of the microscopic structure of the molecules in solvent. It is an extremely difficult probelm 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 simumaltion techniques is 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, to which the thermodynamic limit is concerned. The semi-microscopic approach based on the Poisson-Boltzmann equation and the scaled particle theory deserves to draw attention from such a view point.1) Inspite of the oversimplification employed for the model of solvent, the method could have succeeded to reproduce fundamental characteristics of the solvation thermodynamics of a protein, including the cold denaturation. An well-addressed weakness of the treatment is the less sophisticated representation of the microscopic structure of solvent water. The extended RISM theory has potential capability of overcoming the problem at least in the level of microscopic description based on the pair correlation functions. Ovbious 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 based on the two theoretical tools: extended RISM and the scaled particle theory (SPT). 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 Calculation of Hydration Free Energy for a Solute with Many Atomic Sites Using the RISM Theory: Robust and Efficient Algorithm

Masahiro KINOSHITA *(Kyoto Univ.)*, **Yuko OKAMOTO and Fumio HIRATA**

[*J. Comput. Chem.* **18**, 1320 (1997)]

We have developed an algorithm for solving the reference interaction site model (RISM) equations for water near a solute molecule with many atomic sites (interaction sites). It is a hybrid of the Newton-Raphson and Picard methods which is judiciously constructed. Various considerations are given so that the computer time can be saved as greatly as possible. The robustness and high efficiency of the algoritm has been demonstrated for calculating hydration free energies of Met-enkephalin (a peptide with 75 sites) with different conformations. The Jacobian matrix is treated as part of the input data, and it has been found that the same matrix can be used for a considerably large set of different conformations of the solute molecule.

I-R-2 Solvation Structure and Stability of Peptides in Aqueous Solutions Analyzed by the Reference Interaction Site Model Theory

Masahiro KINOSHITA *(Kyoto Univ.)*, **Yuko OKAMOTO and Fumio HIRATA**

[*J. Chem. Phys.* **107**, 1586 (1997)]

We report results of numerical analyses on solvation structure and conformational stability of a dipeptide and Met-enkephalin in the extended simple point charge (SPC/E) model water. The reference interaction site model (RISM) theory is fully solved using our robust, highly efficient algorithm. It is shown that water structure near the peptides and the hydration free energy are greatly dependent on the peptide conformations. Stability of Met-enkephalin is examined in terms of the total energy defined as the sum of the conformational energy and the hydration free energy of the peptide. We test several different conformations including that with the minimum energy in gas phase, which takes rather compact form due to an intramolecular hydrogen bond. It is shown that a fully extended conformation has the highest stability in water. Our results are in qualitative accord with the recent nuclear magnetic resonance

(NMR) experiments which suggest fully extended conformations with large fluctuations for the solution structure of the peptide. A conformation which is similar to that obtained from the NMR experiments in miceller solutions, is much less stable when it is put in water. Thus, the peptide conformations are greatly sensitive to microscopic solvent environment, and any native treatment of the solvent such as the continuum model will end in failure.

I-R-3 First-Principle Determination of Peptide Conformations in Solvents: Combination of Monte Carlo Simulated Annealing and RISM Theory

Masahiro KINOSHITA *(Kyoto Univ.)*, **Yuko OKAMOTO and Fumio HIRATA**

[*J. Am. Chem. Soc.* **120**, 1855 (1998)]

This paper contributes to development of a microscopic approach to predicting stable conformations of proteins in solvent. We report results of the first attempt to combine Monte Carlo simulated annealing, a powerful conformational sampling technique, and the reference interaction site model (RISM) theory, a statistical-mechanical treatment for molecular fluids. In solvent the key function is the total energy defined as the sum of the conformational energy and the solvation free energy, and the RISM theory is employed to calculate the latter. Starting from an initial conformation given, our computer program samples many conformations, and then finds the conformation with the minimum total energy. Met-enkephalin in the two different solvents, a model water and a simple, repulsive-potential system, are considered. In water the solvation free energy varies greatly from conformation to conformation, while in the simple solvent it remains almost unchanged against conformational changes. In water most of the conformations with larger solvation free energies are strongly rejected and the number of probable conformations is drastically reduced, which is suggestive that Met-enkephalin is forced to take conformations favored by water far more rapidly than in gas phase and in the simple solvent. The set of stable conformations obtained in water are quite different from those in gas phase and the simple solvent: they are characterized by almost fully extended backbone structure with large fluctuations in side-chain structure, which are in qualitatively good agreement with those determined by the recent nuclear magnetic resonance (NMR) experiments.

I-R-4 Calculation of Solvation Free Energy Using RISM Theory for Peptide in Salt Solution

Masahiro KINOSHITA *(Kyoto Univ.)*, **Yuko OKAMOTO and Fumio HIRATA**

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

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

I-R-5 Singular Behavior of the RISM Theory Observed for Peptide in Salt Solution

Masahiro KINOSHITA *(Kyoto Univ.)*, **Yuko OKAMOTO and Fumio HIRATA**

[*Chem. Phys. Lett.* submitted]

We examine the reference interaction site model theory applied to a peptide-salt solution system, with the assumption that a zwitterionic dipeptide (Ala-Ala) is present in NaCl solution at the infinite-dilution limit. For some sets of the parameters in the peptide-cation and peptide-anion potentials, the theory exhibits singular behavior: as the salt concentration decreases, the ionic concentration around the peptide increases and the theory eventually loses its solution. The singularity is interpreted as a signal of the ion condensation. A trend of aggregation of peptide molecules is also found. For other sets of the potential parameters, however, no such singularity occurs. As far as the salt effects are concerned, the qualitative aspects of the conclusionsare somewhat sensitive to the potential parameters employed.

I-R-6 Analysis on Conformational Stability of C-Peptide of Ribonuclease A in Water Using the Reference Interaction Site Model Theory and Monte Carlo Simulated Annealing

Masahiro KINOSHITA *(Kyoto Univ.)*, **Yuko OKAMOTO and Fumio HIRATA**

[*J. Chem. Phys.* submitted]

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

I-R-7 Molecular Theories of Partial Molar Volume

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[*Rev. High Press. Sci. & Tech.* **8**, 96 (1998)]

The theoretical study for response of chemical processes to pressure change requires analyses of the partial molar volume of the chemical species in solution, since the pressure dependence of equilibrium constants is closely related to the difference in the partial molar volumes between reactants and products. The pressure denaturation of protein is one of outstanding properties, which refutes any naive argument concerning 'volume.' According to the most naive argument based on the excluded volume, applying pressure should stabilize its native conformation, because native conformations usually have most compact structure, thereby, the least excluded volume. However, general observations tell us that protein often denatures by applying pressure. How can the paradox be reconciled? The answer to the question may be given by looking at the partial molar volumes, not the 'excluded volume,' before and after the conformational change. The partial molar volume is a thermodynamic response of the chemical potential to pressure change, to which many chemical processes contribute. For instance, some residues in protein may dissociate upon denaturing to release ions, which in turn make partial molar volume less due to so called 'electrostriction' of solvent. If that is the case, protein will unfold by applying pressure. Polar residues will contribute to pressure denaturation in the same direction, if the residues are exposed to solvent upon unfolding. Hydrophobic residues may gives rise to the same effect. It is safe to say that what leads to pressure denaturation of protein are changes in the partial molar volume due to structural change in protein as well as in water. A large volume of experimental works have been devoted to the partial molar volume, but relatively few thoretical studies have been reported. In this report, we have developped two thories for the partial molar volume of protein in water, one based on the extended scaled particle theory and the other based on the Kirkwood-Buff solution theory coupled with RISM equation. Effect of conformational change of a peptide to the partial molar volume is examined by the method.

I-S Spatial and Temporal Density Fluctuation in Molecular Liquids

The latest development in the experimental techniques including the high resolution NMR and a variety of techniques in the time-resolved laser-spectroscopies have revealed the molecular nature of the solvent dynamics around solute or the solvation dynamics, which refuse any naive interpretation based on the continuum models. A microscopic or statistical-mechanical description for the solvation dynamics requires the formulation of the temporal as well as spatial fluctuations of solvent density around solute. A general recipe to such a problem is to use the generalized Langenvin equation (GLE). The GLE in principle gives the dynamics of a system in any resolution in space and time depending on the level of projection. However, its actual usefulness for a problem is largely determined by a choice of dynamic variables onto which other degrees of freedom are projected. It is the pair correlation functions which researves the microscopic nature of the system and yet tractable within the current development in the statistical-mechanical theory of liquids. A natural choices of the dynamic variables which lead to the density-density pair correlation function as an important ingredient in the dynamical equations is a set of the collective density field and its conjugate momentum density field. Such a choice leads to a Smoluchowsky-Vlasov type diffusion equation in the overdamped limit. As to the model for molecular diffusion in polar liquids, there are two quite different point of view. One is the traditinal rot-translational model1) and the other the interaction-site description which sees the diffusion of a molecule as a correlated motion of each atoms (sites).2,3) The interaction-site description employes the site-site Ornstein-Zernike (SSOZ) equation (or RISM equation) in order to represent the site-site direct correlation functions, which proves to be successful in a variety of application to molecualr liquid including water.3)

In what follows, the latest progress which we have made in the theory of the structure and dynamics of molecular liquids is reviewed. We also report our effort to formulate the non-equlibrium free energy profile along a solvent coordinate based on the extended RISM theory, which has played an essential role in the Marcus theory of the electron transfer reaction.

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I-S-1 Interaction-Site-Model Description of Collective Excitations in Classical Molecular Fluids

Song-Ho CHONG *(Kyoto Univ.)* **and Fumio HIRATA**

[*Phys. Rev. E* **57**, 1691 (1998)]

We describe a molecular theory for liquid dynamics which provides a method for calculating dynamical correlation functions of classical molecular fluids. The theory is based on the generalized Langevin equation and on the interaction-site model for molecular liquids. A simple model for memory functions is developed by generalizing the conventional one which has been successfully applied to monatomic systems. The theory is applied to the calculation of longitudinal current spectra of a model diatomic liquid, and collective excitations in this solvent are investigated. We also clarify how these excitations originate from the translational and rotational motions of molecules.

I-S-2 Dynamics of Solvated Ion in Polar Liquids: An Interaction-Site-Model Description

Song-Ho CHONG *(Kyoto Univ.)* **and Fumio HIRATA**

[*J. Chem. Phys.* **108**, 7339 (1998)]

We present a molecular theory for friction coefficient of an ion based on the interaction-site model for molecular liquids and on the mode-coupling theory. The ionic friction is described in terms of response of collective excitations in solvent to a solute displacement, and the resultant formula expresses the friction as an amount of the energy dissipated during the relaxational processes after the solute perturbation. Utilizing this view point, the ionic friction is shown to be naturally decomposed into hydrodynamic, dielectric and their coupling contributions. It is demonstrated from theoretical calculations of the ionic frictions that both of classical pictures, the solventberg and dielectric friction pictures, are responsible for large frictions of small ions and that the coupling term, which has been disregarded in theoretical considerations so far, should also be properly taken into account in dealing with small ions.

I-S-3 Interaction-Site Representation for Collective Excitations in Diatomic Dipolar Liquid

Song-Ho CHONG *(Kyoto Univ.)* **and Fumio HIRATA**

[*J. Mol. Liq.* **77**, 105 (1998)]

We describe a molecular theory for solvent dynamics which provides a method for calculating the dynamic structure factors of molecular fluids. The theory is based on the generalized Langevin equation and on the interaction-site model for molecular liquids. A simple approximation scheme for the memory function is developed by generalizing the conventional one which has been successfully applied to monatomic liquids. The theory is applied to the calculation of longitudinal current spectra of a diatomic dipolar liquid, and collective excitations in this solvent are studied. The paper clarifies how these excitations originate from the translational and rotational motions of molecules.

I-S-4 Effect of Molecular Symmetry on Electrical Potential Fluctuations of Solvent Around Solute in Polar Liquid

Song-Ho CHONG *(Kyoto Univ.)* **and Fumio HIRATA**

[*Chem. Phys. Lett.* **293**, 119 (1998)]

We discuss how the asymmetry structure in solvent and solute affects the free energy profile governing electrical potential fluctuations of solvent around solute and characteristic parameters relevant to electron transfer reactions in solutions using the recently developed method based on the integral equation theory called ex-RISM (the extended reference interaction-site method). Since ex-RISM is inherently a nonlinear theory, we can shed some light on the possible nonlinear effects in electrical potential fluctuations.

I-S-5 Mode-Coupling Theory for Molecular Liquids Based on the Interaction-Site Model

Song-Ho CHONG *(Kyoto Univ.)* **and Fumio HIRATA**

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

I-S-6 Time-Correlation Functions in Molecular Liquids Studied by the Mode-Coupling Theory Based on the Interaction-Site Model

Song-Ho CHONG *(Kyoto Univ.)* **and Fumio**

HIRATA

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

I-T Liquid-Solid Interface

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

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

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

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I-T-1 Theoretical Study for Water Structure at Highly Ordered Surface: Effect of Surface Structure

Ryo AKIYAMA and Fumio HIRATA

[*J. Chem. Phys.* **108**, 4904 (1998)]

Liquid structures of water at electrode-solution interface were investigated by RISM integral equation, putting special stress on the effect of surface structure. Two types of surface geometry were examined: Au(111)-like geometries which is characterized by the threefold hollow sites in which a water molecule can fit, and flat-like surface geometry. The orientation of water molecules in the vicinity of surface depends strongly on the surface structure. Especially, the difference is significant in the case of negatively charged surface. At Au (111)-like surface with negative charges, angles between the surface normal and both of the two O-H vectors are around 108 degree. The result agrees with that proposed experimentally by surface enhanced infrared absorption spectroscopy (SEIRAS) applied to Au(111) surface in aqueous solution of perchloric acid. On the other hand, in the case of flat-like surface the angle between the surface normal and one of the O-H vector is 180 degree, H-atom is available for hydrogen-bonding with bulk water. In the present study, the hydrogen end of water becomes more oriented toward the solution phase above the potential of zero charge (pzc). Those features qualita- tively agree with results proposed by the SEIRAS experiment. However, the orientation of water molecules undergoes significant changes due to the coadsorption of perchlorate ion at a surface with very positive potential.

I-T-2 Solution of the Three-Dimensional RISM/HNC Equations for SPC Water by the Modified Method of Direct Inversion in the Iterative Subspace

Andriy F. KOVALENKO, Seiichiro TEN-NO and

Fumio HIRATA

[*J. Comput. Chem.* submitted (1998)]

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

I-T-3 Three-Dimensional Density Profiles of Water in Contact with a Solute of Arbitrary Shape: A RISM Approach

Andriy F. KOVALENKO and Fumio HIRATA

[*Chem. Phys. Lett.* **290**, 237 (1998)]

We obtain three-dimensional density profiles of interaction sites of a molecular liquid in an external field by generalizing the solute-solvent equation of the Reference Interaction Site Model (RISM) at infinite dilution. The equation complemented with the analogue of the hypernetted chain (HNC) closure is solved on a three-dimensional grid by employing the dynamic relaxation technique. The distribution of water, represented by the Simple Point Charge (SPC) model, around the central water molecule is obtained and discussed. The water density profiles near a (111) FCC crystalline surface are studied. The preferential location and orientation of adsorbed water molecules are discussed.

I-T-4 Extended States of a Shallow Donor Located near a Semiconductor-Insulator Interface

Andriy F. KOVALENKO

[*Intern. J. Quant. Chem.* in press (1998)]

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

I-T-5 The Structure and Adsorption of the Four Bonding Sites Model for Associating Fluids in Disordered Porous Media from Replica Ornstein-Zernike Integral Equation Theory

Andriy F. KOVALENKO and Orest PIZIO
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[*J. Chem. Phys.* **108**, 8651 (1998)]

We have studied a model for an associating fluid in which each of the particles have four sites available for bonding, thus a network of bonds can be formed. This fluid intrinsically possesses liquid-gas transition in the absence of any long-range nonassociative interactions. The model is considered in a disordered porous media that corresponds to an equilibrium configuration of hard spheres. The model is investigated by means of the associative extension of Replica Ornstein-Zernike (ROZ) equations, with the Percus-Yevick (PY) and hypernetted chain (HNC) approximations. Those are supplemented by the ideal network approximation. We have obtained the pair distribution functions and the structure factors of the model. We have obtained the adsorption isotherms using a system of hard spheres adsorbed in a hard sphere matrix as a reference. The associative contribution is obtained similarly to Wertheim's thermodynamic perturbation theory, however, with monomer fraction that follows from the ROZ equations. The liquid-vapor coexistence curve has been obtained complementing the adsorption isotherms by Maxwell construction. We have obtained that with increasing matrix density the critical temperature, if scaled w.r.t.the bulk value, decreases for few percent. The critical density is more sensitive to the density of adsorbent, it substantially decreases with increasing matrix density. We discuss the prepeak on the structure factor at small wave vectors in the adsorbed network-forming fluid at fixed chemical potential dependent on matrix density.

I-U Dimensional Crossovers in Doped Ladder Systems, Organic Conductors and Cuprate Superconductors

Electronic states in pure one dimension and those in two or three dimensions are very different from each other. In many organic conductors and copper oxides, dimensionality is controlled by applying external or chemical pressure. The induced dimensional crossovers are classified by what kind of transverse coherence is restored by increasing dimensionality, i.e., one-particle coherence or two-particle coherence. Which coherence is restored depends on the asymptotic property of the corresponding one-dimensional system. For example, the Tomonaga-Luttinger liquid is known to be unstable against interchain hopping since the transverse one-particle coherence is easily restored. However, in some other one-dimensional phases, the transverse one-particle process is strongly suppressed by electron correlation, and then the transverse two-particle coherence is relatively easily restored. One example is the doped ladder system, $Sr_{14-x}Ca_xCu_{24}O_{41}$, where the spin gap suppresses the transverse one-particle coherence and the two-particle crossover is then accompanied by the superconducting transition. Another example is the quasi-one-dimensional organic conductor, $(TMTTF)_2X$, where the charge gap suppresses the transverse one-particle coherence and the two-particle crossover is then accompanied by the antiferromagnetic transition. More interestingly, the high-T_c copper oxide, $Bi_2Sr_2CaCu_2O_8$, has a partially flat Fermi surface (thus dimensionality depends on the momentum), which anisotropically suppresses one-particle coherence and induces a pseudogap.

I-U-1 Spin Gap and Superconductivity in Weakly Coupled Ladders: Interladder One-Particle vs. Two-Particle Crossover

Jun-ichiro KISHINE and Kenji YONEMITSU

[*J. Phys. Soc. Jpn.* **66**, 3725 (1997)]

Effects of the interladder one-particle hopping, t , on the low-energy asymptotics of a weakly coupled Hubbard ladder system have been studied, based on the perturbative renormalization-group approach. We found that for finite intraladder Hubbard repulsion, U, there exists a crossover value of the interladder one-particle hopping, t_c. For $0 < t < t_c$, the spin gap metal (SGM) phase of the isolated ladder transits at a finite transition temperature, T_c, to the d-wave superconductor (SCd) phase via a two-particle crossover. In the temperature region, $T < T_c$, interladder *coherent Josephson tunneling* of the Cooper pairs occurs, while the interladder coherent one-particle process is strongly suppressed. For $t_c < t$, around a crossover temperature, T_{cross}, the system crosses over to the two-dimensional (2D) phase via a one-particle crossover. In the temperature region, $T < T_{cross}$, the interladder coherent band motion occurs.

I-U-2 One-Particle vs. Two-Particle Crossover in Weakly Coupled Hubbard Chains and Ladders: Perturbative Renormalization Group Approach

Jun-ichiro KISHINE and Kenji YONEMITSU

[*Int. J. Mod. Phys. B* in press]

Physical nature of dimensional crossovers in weakly coupled Hubbard chains and ladders has been discussed within the framework of the perturbative renormalization-group approach. The difference between these two cases originates from different universality classes which the corresponding isolated systems belong to.

I-U-3 Dimensional Crossovers in the Doped Ladder System: Spin Gap, Superconductivity and Interladder Coherent Band Motion

Jun-ichiro KISHINE and Kenji YONEMITSU

[*J. Phys. Soc. Jpn.* **67**, 1714 (1998)]

Based on the perturbative renormalization group (PRG) approach, we have studied dimensional crossovers in Hubbard ladders coupled via weak interladder one-particle hopping, t . We found that the one-particle crossover is strongly suppressed through growth of the intraladder scattering processes which lead the isolated Hubbard ladder system toward the spin gap metal (SGM) phase. Consequently when t sets in, there exists, for any finite intraladder Hubbard repulsion, $U > 0$, the region where the two-particle crossover dominates the one-particle crossover and consequently the d-wave superconducting transition, which is regarded as a bipolaron condensation, occurs. By solving the scaling equations for the interladder one-particle and two-particle hopping amplitudes, we give phase diagrams of the system with respect to U, t_0 (initial value of t) and the temperature, T. We compared the above dimensional crossovers with those in a weakly coupled chain system, clarifying the difference between them.

I-U-4 Antiferromagnetic Phase Transition and Crossover to Fermi Liquid Phase in a Weakly Coupled Half-Filled Chain System

Jun-ichiro KISHINE and Kenji YONEMITSU

[*J. Phys. Soc. Jpn.* **67**, 2590 (1998)]

Effects of the intrachain electron-electron umklapp process and the interchain one-particle hopping, t , in a weakly coupled half-filled chain system have been studied, based on the perturbative renormalization-group approach. By solving the scaling equations, we found that the intrachain umklapp process strongly suppresses an interchain one-particle process and causes a finite critical value for t , t_c. For $t < t_c$, as the temperature decreases, the system undergoes a phase transition into an antiferromagnetic long-range-ordered phase at a transition temperature T_N which increases with the increasing t . On the other hand, for $t > t_c$, the system undergoes a crossover to the Fermi liquid phase where the interchain coherent propagation of quasi-particles occurs.

I-U-5 Effects of Dimerization and Interchain One-Particle Hopping in a Weakly Coupled Dimerized Chain System at Quarter Filling

Jun-ichiro KISHINE and Kenji YONEMITSU

[*Synth. Met.* submitted]

Effects of the intrachain dimerization and the interchain one-particle hopping, t_b, in a quasi-one-dimensional dimerized chain system at quarter filling have been studied, based on the perturbative renormalization group (PRG) approach. Based on the results, we discuss difference in the low-energy properties between TMTTF and TMTSF compounds.

I-U-6 Geometry, Universality and Dimensional Crossovers in Weakly Coupled One-Dimensional Conductors

Jun-ichiro KISHINE and Kenji YONEMITSU

[*Synth. Met.* submitted]

We discuss dimensional crossover phenomena in weakly coupled one-dimensional conductors, in terms of the universality classes of the corresponding isolated one-dimensional systems.

I-U-7 Renormalization-Group Study of Competition between Density Waves and Pairing in Quasi-One-Dimensional Electron Systems

Kenji YONEMITSU

[*Synth. Met.* submitted]

We study crossover from the doped two-leg ladder system to a quasi-one-dimensional system by an inter-ladder one-particle process and stability of the superconductor phase, using a renormalization-group method and differentiating the contributions from the particle-particle channel and those from the particle-hole channel. Effects of electron-$2k_F$ phonon and electron-$4k_F$ phonon couplings are also investigated.

I-U-8 Anisotropic Suppression of Quasiparticle Weight in Two-Dimensional Electron System with Partially Flat Fermi Surface: Two-Loop Renormalization-Group Analysis

Jun-ichiro KISHINE and Kenji YONEMITSU

[*Phys. Rev. B* submitted]

Two-loop renormalization-group analysis for a two-dimensional electron system with a partially flat Fermi surface has been carried out. We found that, irrespective of pairing mechanism, the quasiparticle weight is anisotropically suppressed due to logarithmically singular processes in the flat regions of the Fermi surface. When the energy scale decreases, the quasiparticle weight is the most strongly suppressed around the center of the flat region, which qualitatively agrees with the anisotropic pseudogap behavior suggested through the angle-resolved photoemission spectroscopy experiments for underdoped $Bi_2Sr_2CaCu_2O_8$.

I-V Magnetic Properties of Metal-Assembled Complexes with Two Different-Dimensional Bands

Antiferromagnetism and superconductivity are realized in strongly correlated, organic materials. In κ-(BEDT-TTF)$_2$*X*, the two-dimensional quarter-filled HOMO band is effectively regarded as a half-filled band due to strong dimerization. Strong dimerization is realized in the metal-assembled complex, $Me_4Z[Pd(dmit)_2]_2$, also. In the latter, however, there are a rather one-dimensional LUMO band and a two-dimensional HOMO band, both of which are largely split due to the dimerization. So far, we do not know which band is responsible to the pressure-induced metal and superconductor phases. Meanwhile, the phase diagram is richer than that of κ-(BEDT-TTF)$_2$*X* in that applied pressure induces a metal or superconductor phase and then an insulator phase again. Whether the origins of the two insulator phases are the same or not is currently of particular interest. We study this problem using a mean-field theory and a strong-coupling expansion as a first step, showing the two phases may correspond to two possible magnetic phases. We have found the exchange interactions are not simple as one usually expects. For example, some exchange interaction is ferromagnetic due to the mechanism which causes flat-band ferromagnetism. Whether the exchange interaction is ferromagnetic or antiferromagnetic depends on the symmetry of the molecular orbitals.

I-V-1 On the Effects of On-Site Coulomb Interaction in Strongly Dimerized Two Band Systems

Hiori KINO *(JRCAT-ATP)*, **Tsuyoshi MIYAZAKI** *(NRIM)*, **Michiyasu MORI and Kenji YONEMITSU**

[*Proceedings of the JRCAT Conference*]

We consider the strongly dimerized two-band organic solids, $Me_4Z[M(dmit)_2]_2$ (dmit=2-thioxo-1,3-dithiole-4,5-dithiolate), where Z = N, P, As, Sb and M = Ni, Pd (β polytype in the Pd(dmit)$_2$ salts). A phase diagram is shown in the plane of the on-site Coulomb interaction and the level splitting between the HOMO and the LUMO of the M(dmit)$_2$ molecule, based on the results of the Hartree-Fock (HF) approximation. The nature of the phase transition is discussed. The results of the exact diagonalization for small clusters is also presented to check the validity of the HF approximation.

I-V-2 Possible Magnetic Phases in Two-Band Systems with Different Dimensionality

Michiyasu MORI, Kenji YONEMITSU and Hiori KINO *(JRCAT-ATP)*

[*Synth. Met.* submitted]

The ground states of the molecular conductors Me$_4$*Z*[M(dmit)$_2$]$_2$, which have strong dimerization and two bands with different dimensionality, have been studied based on the Hartree-Fock approximation. The results indicate that two different magnetic orders appear depending on both the energy difference between the two bands and the strength of the Coulomb interaction. To clarify the origin of the magnetic orders, exchange interactions between dimers have been calculated within the second-order perturbation theory with respect to the inter-dimer transfer integrals. We have found that the different magnetic orders are due to the different symmetry of the molecular orbitals.

I-V-3 Effective Exchange Interactions in Dimerized Systems

Michiyasu MORI and Kenji YONEMITSU

In our previous work, it has been clarified that the ground states of Pd(dmit)$_2$ salts have two different antiferromagnetic (AF) orders depending on both the energy difference between molecular orbitals and the strength of the Coulomb interaction. These orders have uniform charge density, i.e., 0.5 electron per site, and it can be considered as AF orders between dimers. Thus, we have calculated the exchange interactions between dimers within the second-order perturbation theory with respect to the inter-dimer transfer integrals. The results indicate that one magnetic order is dominated by HOMO (highest occupied molecular orbital) and the other originates from LUMO (lowest unoccupied molecular orbital). The molecular orbitals HOMO and LUMO have different symmetry and result in the different magnetic orders. In the case of LUMO, interestingly, the ferromagnetic coupling is also possible in a particular direction. The origin of such ferromagnetic exchange interaction is equivalent to the mechanism of flat-band ferromagnetism. Our calculation is also applicable to BEDT-TTF salts and other dimerized systems.

I-V-4 From Possible Magnetic Orders to Quantum Disorder

Michiyasu MORI and Kenji YONEMITSU

The anion radical salt (Et$_x$Me$_{4-x}$*Z*)[Pd(dmit)$_2$]$_2$ exhibits a metal (superconductor)-insulator transition at low temperature and under pressure. For such phase transitions, cation effects play significant roles. The system with cation Me$_4$P is always an insulator even under pressure, while the system with cation Et$_2$Me$_2$P becomes a superconductor under pressure, for example. At ambient pressure, however, the system with any cation behaves as an insulator. Thus, in this present paper, the cation effects in the insulator phases have been investigated. The magnetic properties of Pd(dmit)$_2$ salts can be described by a dimer spin model, in which the dimer is a site for the localized spins. The exchange interactions between dimers are calculated in our previous papers. We have found that the cation effect is considered as the frustration for the spin system on the triangular lattice. Then, we have calculated the stability of antiferromagnetic (AF) orders based on the spin wave approximation for the frustrated spin systems. The results indicate that in the case of Me$_4$P the AF order is stable, while in the case of Et$_2$Me$_2$P the AF order is unstable and goes into a quantum disordered phase because of the frustration. These results are consistent with the experiment of the magnetic susceptibility at ambient pressure.

I-W Metal-Insulator and Superconducting Transitions in Strongly Correlated Electron Systems Coupled with Localized Spins or Phonons

Electronic states are influenced by the presence of local degrees of freedom such as localized spins or phonons. Especially, when the conduction electrons are confined in low dimensions and strongly correlated, the problems are highly nontrivial. Here, we study the effect of exchange coupling with localized spins in a one-dimensional quarter-filled system (Heisenberg-Kondo lattice) and the effect of electron-phonon coupling in a two-dimensional doped antiferromagnet (Holstein-Hubbard polaron system). The former system corresponds to the one-dimensional π-*d* electron system, CoPc(AsF$_6$)$_{0.5}$, while the latter system is compared with the high-T_c copper oxides. In the former system, the exchange coupling alone does not produce an insulator phase, but long-range repulsion can induce an insulator phase with the help of the exchange coupling at least when the localized spins are antiferromagnetically ordered. In the latter system, the electron-phonon coupling produces self-trapped polarons which attract each other and form *d*-wave pairs. Berry phases are convenient tools to explain the symmetry, quantum numbers and statistics of polarons and polaron pairs. The properties of these polarons are very different from those of ordinary polarons and may explain the strange isotope effect observed in the high-T_c copper oxides.

I-W-1 Conductivity and Magnetic Properties of One-Dimensional Heisenberg-Kondo Lattice

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Using the one-dimensional quarter-filled Heisenberg-Kondo lattice model for a π-*d* electron system, CoPc$(AsF_6)_{0.5}$, we study the effects of long-range Coulomb interaction among π electrons on the conductivity. The density-matrix renormalization-group method is employed. As a first step, we regard the localized spins of *d* electrons as classical ones, and then, as quantum $S = 1/2$ spins, which are coupled antiferromagnetically with each other. In the former case, *d* electrons produce a static staggered magnetic field for π electrons. It is pointed out that the next-nearest-neighbor repulsion among π electrons and the magnetic coupling between π and *d* electrons are essential to open a charge gap.

I-W-2 Superconductivity and Magnetism in Quasi-One-Dimensional Two-Band Systems

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[*Rev. High Pressure Sci. Technol.* **7**, 490 (1998)]

We study crossovers from one to quasi-one dimensions in doped two-leg ladder systems, using a renormalization group method. When quasi-one dimensionality is regarded as controlled by incomplete interference between the Cooper and Peierls channels, we obtain spin-density wave, *d*-wave superconductor, and metal phases with decreasing dominance of the Peierls channel. When transverse single-particle hopping is treated perturbationally, we obtain a one-particle crossover from incoherent to coherent transverse motion for weak interaction and a two-particle crossover from short- to long-range ordering of a *d*-wave superconductor for strong interaction. We also study a magnetic property in a doped Heisenberg-Kondo chain, using the exact diagonalization method. A fully saturated ferromagnetism in the ferromagnetic Kondo chain is destroyed by rather weak antiferromagnetic Heisenberg coupling between localized $S = 1/2$ spins.

I-W-3 Berry Phases and Pairing Symmetry in Holstein-Hubbard Polaron Systems

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[*Phys. Rev. B* in press]

We study the tunneling dynamics of dopant-induced hole polarons which are self-localized by electron-phonon coupling in a two-dimensional antiferromagnet. Our treatment is based on a path integral formulation of the adiabatic (Born-Oppenheimer) approximation, combined with many-body tight-binding, instanton, constrained lattice dynamics, and many-body exact diagonalization techniques. The applicability and limitations of the adiabatic approximation in polaron tunneling problems are discussed in detail and adiabatic results are compared to exact numerical results for a two-site polaron problem. Our results are mainly based on the Holstein-*tJ* and, for comparison, on the Holstein-Hubbard model. We also study the effects of 2nd neighbor hopping and long-range electron-electron Coulomb repulsion. The polaron tunneling dynamics is mapped onto an effective low-energy Hamiltonian which takes the form of a fermion tight-binding model with occupancy dependent, predominantly 2nd and 3rd neighbor tunneling matrix elements, excluded double occupancy, and an effective intersite charge interactions. Antiferromagnetic spin correlations in the original many-electron Hamiltonian are reflected by an attractive contribution to the 1st neighbor charge interaction and by Berry phase factors which determine the signs of effective polaron tunneling matrix elements. In the two-polaron case, these phase factors lead to polaron pair wave functions of either $d_{x2\text{-}y2}$-wave symmetry or *p*-wave symmetry with zero and nonzero total pair momentum, respectively. Implications for the doping dependent isotope effect, pseudo-gap and T_c of a superconducting polaron pair condensate are discussed and compared to observed properties of the cuprate high-T_c materials.

I-X Coexistence of or Competition between Different Density Waves in One-Dimensional Quarter-Filled Organic Conductors

Quasi-one-dimensional organic conductors show a variety of phases due to the instability of a metallic state described by the Fermi liquid theory. Many phases are understood within mean-field theories for tight-binding models with short-range repulsion. When coexistence of purely electronic spin-density and charge-density waves was suggested in $(TMTSF)_2PF_6$ by X-ray experiments two years ago for the first time, many scientists regarded this phenomenon as mysterious since one usually expects only one type of long-range order except $4k_F$ charge ordering. We show that this is due to a cooperative effect of long-range repulsion (especially, next-nearest-neighbor repulsion) which are usually neglected and dimerization which lowers the symmetry of electronic states. Such importance of long-range repulsion has been pointed out for the charge ordering in a quarter-filled π-electron system, $(DI\text{-}DCNQI)_2M$ (M = Li, Ag), and for the insulator phase in a quarter-filled π-*d* electron system, CoPc$(AsF_6)_{0.5}$. For $(DCNQI)_2M$ (M = Li, Ag), we apply the full configuration interaction method to an effective

Hamiltonian whose parameters are derived from the ab initio molecular orbital theory. Antiferromagnetic correlation and $4k_F$ charge ordering in these systems are reproduced.

I-X-1 Coexistence of SDW and Purely-Electronic CDW in Quarter-Filled Organic Conductors

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[*J. Phys. Soc. Jpn.* **67**, 1098 (1998)]

We have performed a mean field calculation in order to determine the ground state of a modified Hubbard model of a quarter-filled one-dimensional chain. It is found that the coexistence of $2k_F$ spin density wave (SDW) and purely-electronic $2k_F$ charge density wave (CDW) is realized due to the effect of next-nearest-neighbor Coulomb repulsion. Phase diagrams are obtained as the values of nearest- and next-nearest-neighbor Coulomb interaction energies are varied. Competition between the two coexistent states with $2k_F$ CDW and with $4k_F$ CDW is revealed, which gives a first order transition. Our result supports the X-ray result confirming the presence of a coexisting phase of purely-electronic $2k_F$ CDW and $2k_F$ SDW in $(TMTSF)_2PF_6$, a quarter-filled one-dimensional chain in terms of holes.

I-X-2 Coexistence of SDW and Purely-Electronic CDW in Quarter-Filled Organic Conductors at Finite Temperatures

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[*Synth. Met.* submitted]

Recently an X-ray experiment reported a coexisting phase of purely-electronic $2k_F$ charge density wave (CDW) and the conventional $2k_F$ spin density wave (SDW) in $(TMTSF)_2PF_6$. In order to understand such coexistence, we have performed a mean-field calculation for a Hubbard-type model of a quarter-filled one-dimensional chain. It is found that the coexistence of $2k_F$ SDW and *purely-electronic* $2k_F$ CDW is realized due to the effect of next-nearest-neighbor Coulomb repulsion. Phase diagrams are obtained as a function of nearest- and next-nearest-neighbor Coulomb interaction energies. Competition between the two coexistent states with $2k_F$ CDW and with $4k_F$ CDW is revealed, which gives a first order transition. It turns out that the internal degrees of freedom inside a dimer (consisting of two TMTSF molecules) play an important role. Our result supports the X-ray result of a coexisting phase in $(TMTSF)_2PF_6$. When the coexistent state with $2k_F$ CDW is realized, the critical temperature for $2k_F$ SDW is slightly higher than that for $2k_F$ CDW. These two transition temperatures are close enough to explain the experimental result.

I-X-3 Exact Diagonalization Study of $(DCNQI)_2M$ (M = Li, Ag) Clusters Based on Ab Initio Molecular Orbital Parameters

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[*Chem. Phys. Lett.* submitted]

We study electronic states of the $(DCNQI)_2M$ (M = Li and Ag) salts based on the full configuration interaction (FCI) method using effective Hamiltonians derived from the ab initio molecular orbital theory. FCI results of the DCNQI tetramer and octamer models indicate that the ground state has the antiferromagnetic and charge ordering correlations. It corresponds to the $2k_F$ spin density wave and $4k_F$ charge density wave states (SDW and CDW). In the octamer model, it is also found that some low-lying excited states have similar spin-flipped CDW correlations and the antiferromagnetic correlation is weakened.

I-Y Electron Correlation and New Photoinduced Phenomenon in Polymers

Electron correlation is important in conducting polymers also, in order to understand the relation between electron correlation and the strength of dimerization, and to understand the symmetry of the lowest excited state. The latter is crucial to luminescence and its applications to electronic devices. First, we study the effect of the off-diagonal part of the electron-electron interaction on the ground state and on the coherence length, going beyond a mean-field theory. Next, we point out a possibility of negative polarizability in photoexcited polymers of nondegenerate ground states which have biexcitons. Here, the proximity of the mid-gap states is crucial. Note that negative polarizability is impossible in a gas or condensed matter in an equilibrium state, but it is not prohibited in principle in a molecule in an excited state.

I-Y-1 Effect of Electron Correlation on Competition between BOW and SDW in Polymer

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Because π electrons in polymers possess a broad band, the off-diagonal part of the electron interaction, which is omitted in the extended Hubbard model, plays an essential role in the competition between bond-order waves (BOWs) and spin-density waves (SDWs). Our study, which goes beyond the extended Hubbard model and the Hartree-Fock approximation, shows that this competition depends on the range of the electron interaction; a short interaction range, where the off-diagonal part is more effective, is in favor of SDW. It is also shown that the correlation effect works against the exchange effect in building up the SDW.

I-Y-2 Off-Diagonal Interactions and Spin-Density Waves in Polymers

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[*Phys. Rev. B* in press]

In order to clarify the effects of electron interaction on the competition between SDW (spin-density wave) and BOW (bond-order wave), the existing theories are improved in two aspects: (1) The electron interaction in polymers, which possess a broad band, is described by screened Coulomb potential rather than the extended Hubbard model, which is a good approximation only for narrow-band systems. (2) A spin-dependent CBF (correlated-basis-function) method is developed to calculate the correlation effect, which goes beyond the HF (Hartree-Fock) approximation. Our study shows that the off-diagonal interaction substantially influences the competition so that shortening of the interaction range greatly enhances the SDW; meanwhile the correlation effect promotes the BOW against the SDW.

I-Y-3 A Correlated-Basis-Function Study of SDW in Polymers

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[*Synth. Met.* submitted]

We study SDW in polymers, using screened Coulomb potential to describe full electron interaction in the broad-band systems and developing a spin-dependent correlated-basis-function method to handle the correlation effect. The SDW is shown to be sensitively enhanced with shortening interaction range and suppressed by the correlation effect.

I-Y-4 Making a Molecule with Negative Polarizability

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Many novel phenomena have been found in excited states by ultrafast technology. One more is proposed here. The molecular magnetic susceptibility can be positive or negative. But, so far, the electrical susceptibility α of all observed molecules is always positive. Can a molecule with negative α exist? Our study shows it can be realized by photoexcitation, one candidate is the polymer with a bipolaron. It is a new photoinduced phenomenon — photoinduced polarization inversion, an ultrafast process with relaxation time of 2×10^{-13} second. The molecule with negative α possesses anomalous charge transfer, whose direction is opposite to that expected by the Coulomb's Law.

I-Y-5 Polarization and Dissociation of Exciton in Luminescent Polymers

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[*Synth. Met.* submitted]

It is shown in this paper that the exciton in polymers possesses very large polarizability, and when the electric field is strong enough, the exciton in luminescent polymers is dissociated into a pair of charged polarons. This dissociation can quantitatively interpret the experiment that the luminescence of polymer is heavily quenched by strong electric field.