I-P Electronic Structure of a Molecule in Solution

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

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

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

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

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

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

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

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

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I-P-1 Theoretical Study on the Structures and Energies of Acetic Acid Dimers in Aqueous Solution

NAKABAYASHI, Takakazu; SATO, Hirofumi; HIRATA, Fumio; NISHI, Nobuyuki

[*J. Phys. Chem. A* **105**, 245 (2001)]

The effects of hydration on the dimerization energies and structures of acetic acid dimers are studied by the reference interaction site model self-consistent-field (RISM-SCF) method. Comparisons of the RISM-SCF results are also made with those obtained from the self-consistent reaction field (SCRF) methods to examine the dielectric effects of the solvent. The RISM-SCF method predicts the marked stabilization due to solvation in the dimer structures with large dipole moments. From the decomposition analysis of the excess chemical potential, the contribution from the free carbonyl oxygen is found to be much larger than the other atoms for the stabilization of these dimers in aqueous solution. Such a stabilization in the polar dimers is not obtained from the simplest SCRF method that considers only the solute dipole.

I-P-2 Realization of Three-Dimensional Solvation Structures from the Site-Site Radial Distribution Functions in Liquids

SATO, Hirofumi; HIRATA, Fumio

[*Bull. Chem. Soc. Jpn.* **74**, 1831 (2001)]

We propose a new procedure to realize a three-dimensional (3D) solvation structure around a solute molecule from a set of radial distribution functions (RDF), or distance information. The method consists of the minimization of a penalty function defined as the mean-square difference of the solute-solvent interatomic distances obtained from trial 3D configurations and from target RDFs. The hydration structures around several different solute molecules are visualized to demonstrate the method.

The solvation structures realized with the present method correspond to the most plausible solvation structure (MPSS), which looks like a “snap shot” of the molecular dynamics trajectory. However, the MPSS is essentially different from the “snap shot,” since it represents an average configuration, and is therefore an observable quantity. The present procedure was originally developed for analyses of the RDF results obtained from the reference interaction site model (RISM), but can be applied straightforwardly to RDFs from other sources, such as molecular simulations and scattering experiments.

I-P-3 Solvent Effect on the Nuclear Magnetic Shielding: Ab initio Study by the Combined Reference Interaction Site Model and Electronic Structure Theories

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[*J. Chem. Phys.* **115**, 8949 (2001)]

A method for calculating the nuclear magnetic shielding constant of atoms in solution is proposed based on the *ab initio* electronic structure theory combined with the extended reference interaction site model in statistical mechanics for molecular liquids. The method is applied to a water molecule solvated in water, acetone, chloroform, and carbon tetrachloride. The results for solvation effect demonstrate capability to predict the experimental results. The theory provides a tool to investigate the solvent effect on the nuclear magnetic shielding and its temperature dependence from a molecular view point. The theory takes account for effect of the electrostatic interaction on the electronic structure of solute, but disregards the electron overlap. The effect of intermolecular overlap of electron on the nuclear magnetic shieldings is examined using a molecular cluster model.

I-Q Solvation Thermodynamics of Protein and Related Molecules

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

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

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I-Q-1 Hydration Structure and Stability of Met-Enkephalin Studied by a Three-Dimensional Reference Interaction Site Model with a Repulsive Bridge Correction and a Thermodynamic Perturbation Method

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[*J. Chem. Phys.* **113**, 9830 (2000)]

We study the hydration structure and free energy of several conformations of Met-enkephalin in ambient water by employing the one-dimensional (1D) as well as three-dimensional (3D) reference interaction site model (RISM) integral equation theories, complemented by the hypernetted chain (HNC) closure with the repulsive bridge correction (RBC). The RBC contribution to the excess chemical potential of solvation is calculated by means of the thermodynamic perturbation theory (TPT), which crucially reduces computational burden and thus is especially important for a hybrid algorithm of the RISM with molecular simulation. The 3D-

RISM/HNC+RBC-TPT approach provides improved prediction of the solvation thermodynamics and gives a detailed description of the solvation structure of a biomolecule.

The results obtained are discussed and compared to those following from the 1D-RISM/HNC theory. The latter yields physically reasonable results for the conformational stability of biomolecules in solution, which is further improved by adding the 1D-RBC. The modified, 1D-RISM/HNC-RBC-TPT integral equation theory combined with the simulated annealing or generalized-ensemble Monte-Carlo simulation methods is capable of reliable prediction of conformations of biomolecules in solution with due account for the solvent effect at the microscopic level.

I-Q-2 Theoretical Study for Partial Molar Volume of Amino Acids and Poly-Peptides by the Three-Dimensional Reference Interaction Site Model

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[*J. Chem. Phys.* **114**, 9506 (2001)]

We calculate the partial molar volume (PMV) of twenty amino acids in aqueous solution at infinite dilution is by using the Kirkwood-Buff equation and the three-dimensional reference interaction site model (3D-RISM) integral equation theory for molecular liquids. As compared to the conventional, one-dimensional (1D-RISM) approach, the results exhibit drastic improvement for the quantitative agreement with experiment. The deviation from the experimental data, seen for the relatively large amino acids is discussed in terms of the "ideal fluctuation volume" introduced in the previous study based on the 1D-RISM to account for flexibility of solute molecules. Robustness of the new approach is further demonstrated by applying it to the PMV of poly-glutamic acids in aquous solution. The method provides reasonable account for the PMV increase with the chain length, both in a-helical and extended structures, whereas the 1D-RISM approach gives an unnatural decrease of the PMV for the a-helix with a complete turn of the backbone.

I-Q-3 Theoretical Study for Volume Changes Associated with the Helix-Coil Transition of Polypeptides

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[*Biopolymers* **59**, 512 (2001)]

We calculate the partial molar volumes and their changes associated with the coil(extended)-to-helix transition of two types of peptide, glycine-oligomer and glutamic acid-oligomer, in aqueous solutions by using the Kirkwood-Buff solution theory coupled with the three-dimensional reference interaction site model (3D-RISM) theory. The volume changes associated with the transition are small and positive. The volume is analyzed by decomposing it into five contributions following the procedure proposed by Chalikian and Breslauer: the ideal volume, the van der Waals volume, the void volume, the thermal volume, and the interaction volume. The ideal volumes and the van der Waals volumes do not change appreciably upon the transition. In the both cases of glycine-peptide and glutamic acid-peptide, the changes in the void volumes are positive, while those in the thermal volumes are negative, and tend to balance those in the void volumes. The change in the interaction volume of glycine-peptide does not significantly contribute, while that of glutamic acid-peptide makes negative contribution.

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

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

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

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I-R-1 Site-Site Mode-Coupling Theory for the Shear Viscosity of Molecular Liquids

YAMAGUCHI, Tsuyoshi; HIRATA, Fumio

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

A mode-coupling expression for the shear viscosity coefficient of dense molecular liquids based on the interaction site model is presented. It is a natural extension of the corresponding theory for simple liquids, in which the shear stress auto correlation function is described as the linear combination of the bilinear products of the site-site dynamic structure factor. The theory is applied to water at the ambient condition. The agreement between the theory and the computer experiment is fairly good for the simplicity of the theory.

I-R-2 Solute-Shape Dependence in Solvation Dynamics: Investigated by RISM Theory

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OKADA, Tadashi[1]
([1]Osaka Univ.)

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

A combination of the reference interaction-site model (RISM) theory and the site-site Smoluchowski-Vlasov equation has been applied to estimate solute-shape dependence of the dynamic average-energy relaxation of the solute-solvent system in a polar solvent. If the solute became larger, like octapoles, the relaxation got much slower. A plausible mechanism of the relaxation will be discussed.

I-R-3 Nonlinear Response of Solvent Molecules Induced by Instantaneous Change of Solute Electronic Structure: Studied by RISM Theory

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OKADA, Tadashi[1]
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[*J. Mol. Struct.* **565–566**, 31(2001)]

We have applied the reference interaction-site model (RISM) theory for the estimation of the dynamic response function of the average-energy relaxation, $S_S(t)$, of the solute-solvent systems, induced by an instantaneous change of the solute electronic structure in polar solvents. We choose the solutes including square- or cubic-like structures: initially all the atoms are electrically neutral and, then we put δ^+ and δ^- charges instantaneously. For the multipoles $S_S(t)$s show apparent dependence on *d*, which predicts nonlinear response of the solvent, because $S_S(t)$ is a normalized quantity irrespective of δ as far as the linear response of the solvent dynamics is assumed. On the other hand we have previously performed transient hole-burning and time-resolved fluorescence spectroscopy. We have found the difference between the dynamic response functions obtained from spectral widths and that from spectral peak shifts, implying the nonlinear solvent-response, as these two kinds of the response functions should again correspond to each other within a linear response regime. Our present results from the RISM theory can be another indicative to confirm nonlinearity suggested by our experiments. At the moment we ascribe the origin of the nonlinear solvent behavior to the larger local-density fluctuation around the solute.

I-R-4 Average Energy Relaxation and Rearrangement of Solute-Solvent Radial Distribution Function in Solvation Dynamics: A Connection between Spectroscopic Results and RISM Theory

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[*J. Mol. Liq.* **90**, 251(2001)]

We calculate the relaxation dynamics of the average energy of solute-solvent systems as well as time-dependent solute-solvent radial distribution functions by means of the reference interaction-site model (RISM) theory. Compared with the experimental results obtained in our previous work, we suggest that the rearrangement of the further solvation shell could be important for the relaxation dynamics of the inhomogeneous spectral band width observed by means of transient hole-burning and time-resolved fluorescence spectroscopy.

I-S Developing Theories of Liquids and Liquid Mixtures

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

In what follows, we describe our challenges to explore new problems related to liquids and liquid mixtures. The challenge inevitably includes methodological development in the statistical mechanics of liquids.

I-S-1 Integral Equations for Molecular Fluids Based on Interaction Site Model: Density-Functional Formulation

SUMI, Tomonari; IMAI, Takashi; HIRATA, Fumio

[*J. Chem. Phys.* **115**, 6653 (2001)]

An integral equation for rigid-body molecules with respect to site-density distribution function under arbitrary external fields is derived by density-functional theory. Using a grand canonical partition function of molecular systems, we extend original Percus’ idea to molecular fluids. The extended Percus’ idea provides a relation between site-site pair distribution function and site-density distribution function under an external field composed of the site-site interaction potentials of a molecule fixed at the origin. The site-density integral equation combined with the extended Percus' relation to molecular fluids gives a closure relation of reference interaction site model (RISM) equation. The site-site pair distribution functions of homonuclear diatomic Lennard-Jones fluids obtained by the integral equation agree well with those of Monte Carlo simulation.

I-S-2 A Replica Reference Interaction Site Model Theory for a Polar Molecular Liquid Sorbed in a Disordered Microporous Material with Polar Chemical Groups

KOVALENKO, Andriy; HIRATA, Fumio

[*J. Chem. Phys.* **115**, 8620 (2001)]

We develop a replica generalization of the reference interaction site model (replica RISM) integral equation theory to describe the structure and thermodynamics of quenched-annealed systems comprising polar molecular species. It provides a successful approach to realistic models of molecular liquids, and properly allows for the effect of a quenched disordered matrix on the sorbed liquid. The description can be extended to an electrolyte solution in a disordered material containing charged chemical functionalities that determine its adsorption character. The replica RISM equations are complemented with the HNC closure and its partial linearization (PLHNC), adequate to ionic and polar molecular liquids. In these approximations, the excess chemical potentials are derived in a closed analytical form. We extend the description to a quenched-annealed system with soft-core interaction potentials between all species, in which the liquid and matrix equilibrium distributions are characterized in general by two different temperatures. The replica RISM/PLHNC-HNC theory is applied to water sorbed in a quenched disordered microporous network of atoms associated into interconnected branched chains, with activating polar groups grafted to matrix chains. The results are in qualitative agreement with experiment for water confined in disordered materials.

I-S-3 First-Principles Realization of a van der Waals-Maxwell Theory for Water

KOVALENKO, Andriy; HIRATA, Fumio

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

We generalize the van der Waals-Maxwell description of the fluid phase diagram to account for chemical specificities of polar molecular fluids, such as hydrogen bonding in water. The theory is based on the reference interaction site model (RISM) integral equation method in the partially linearized hypernetted chain (PLHNC) approximation. The predictions for the liquid-vapor coexistence of water are in qualitative agreement with molecular simulations. The theory can be extended to electrolyte as well as non-electrolyte solutions, and to ionic liquids.

I-S-4 Thermochemistry of Solvation: A Self-Consistent Three-Dimensional Reference Interaction Site Model Approach

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[*J. Chem. Phys.* **113**, 7458 (2000)]

We developed a self-consistent three-dimensional reference interaction site model integral equation theory with the molecular hypernetted chain closure (SC-3D-RISM/HNC) for studying thermochemistry of solvation of ionic solutes in a polar molecular solvent. It is free from the inconsistency in the positions of the ion-solvent site distribution peaks, peculiar to the conventional RISM/HNC approach and improves the predictions for the solvation thermodynamics. The SC-3D-RISM treatment can be readily generalized to the case of finite ionic concentrations, including the consistent dielectric corrections to provide a consistent description of the dielectric properties of ion-molecular solution. The proposed theory is tested for hydration of the Na^+ and Cl^- ions in ambient water at infinite dilution. An improved agreement of the ion hydration structure and thermodynamics with molecular simulation results is found as compared to the conventional RISM/HNC treatment.