

I-Q Electronic Structure of a Molecule in Solution

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

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

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

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

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

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

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

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

References

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

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

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The electronic and solvation structures of the metal

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

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

I-R Solvation Thermodynamics of Protein and Related Molecules

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

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

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

References

- 1) M. Kinoshita, Y. Okamoto and F. Hirata, *J. Am. Chem. Soc.* **120**, 1855 (1998).
- 2) A. Kitao, F. Hirata and N. Go, *J. Phys. Chem.* **97**, 10231 (1993).
- 3) M. Irisa, K. Nagayama and F. Hirata, *Chem. Phys. Lett.* **207**, 430 (1993).

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

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

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

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

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

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

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

References

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

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

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

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

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

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

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

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

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

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

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

I-T Developing Theories of Liquids and Liquid Mixtures

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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