I-L Electronic Structure of a Molecule in Solution

Chemical reaction is undoubtedly the most important issue in the theoretical chemistry, and the electronic structure is a key to solve the problem. As long as molecules in the gas phase are concerned, the theory for the electronic structure has been enjoying its great success. However, when it comes to molecules in solution, the stage of theory is still an infant. 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 follows;

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

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-L-1 A Quantum Solute-Solvent Interaction Using Spectral Representation Technique Applied to the Electronic Structure Theory in Solution

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In this paper, we present a new approach to treat the electronic structure of a molecule in solution. Unlike the hybrid-type method such as the reference interaction site model self-consistent-field(RISM-SCF) theory, the new approach describes not only the electronic structure of solute but also solute-solvent interactions in terms of the quantum chemistry based on the Hartree-Fock frozen density formulation. In the treatment, the quantum effect due to solvent, including exchange repulsion, is projected on to the solute Hamiltonian using the spectral representation method. The solvent distribution around the solute is handled by the integral equation theory of liquids. As illustrative applications of the approach, the electronic and solvation structure of noble atoms, neon and argon, in liquid neon are studied. We also investigate the electronic structure of an excess electron in liquid helium. The preliminary results demonstrate that the quantum mechanical effect on the electronic and solvation structure of the solute due to solvent molecules is successfully represented by the new method.

I-L-2 Distortion of Electronic Structure in Solvated Molecules: Tautomeric Equilibrium of 2-Pyridone and 2-Hydroxypridine in Water Studied by the RISM-SCF/MCSCF Method

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As well recognized, the electronic structure of a molecule in the solution phase is distorted from that in

the gas phase. We present a new procedure that enables us to partition the electronic distortion energy caused by solvation into the energy contribution of each atom (or each moiety), with which one can evaluate the atomic-level change of electronic structure. In the present study, we combine the procedure with the RISM-SCF method that can treat solvent molecules explicitly. This method is successfully applied to the tautomerization of 2-pyridone in aqueous solution, whose equilibrium is known to show a marked solvation effect, and provides us a new detailed feature of this equilibrium. (1) As expected, electronic structures of oxygen and nitrogen atoms, which are strongly solvated, are distorted significantly. (2) However, the electronic distortion energies of the oxygen and nitrogen atoms are considerably compensated by the microscopic solvation. (3) One of the determining factors of the equilibrium is the carbon atom, with which the oxygen atom is bound, because the electronic distortion cannot be compensated by the microsolvation due to its rather inside position, and (4) the other factor is the distortion energy of the proton that directly relates to the equilibrium probably because the electronic structure changes too much to be compensated by microsolvation. These new findings lead to deep and correct understanding of this equilibrium.

I-L-3 Theoretical Study on Electronic and Solvent Reorganization Associated with a Charging Process of Organic Compounds: II. A New Decomposition Procedure into Electrostatic and Non-Electrostatic Responses

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A new procedure, which enables us to decompose the solvent reorganization energy into electrostatic and nonelectrostatic contributions, is proposed. By using the procedure proposed by us very recently (*J. Phys. Chem. A* **106**, 2300–2304 (2002)), the solvent reorganization process and electronic structures of N,N-dimethylaniline (DMA) and 1,4-dimethoxybenzene (DMB) associated with a charging process in acetonitrile solution are studied at the molecular level on the basis of the ab initio reference interaction site model-self-consistent field (RISM-SCF) method. Differences as well as similarities between the solvation processes of the two molecules are discussed on the basis of the newly proposed method.

I-L-4 Superexchange Electron Tunneling Mediated by Solvent Molecules: Pulsed Electron Paramagnetic Resonance Study on Electronic Coupling in Solvent-Separated Radical Ion

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Nanosecond pulsed electron paramagnetic resonance spectroscopy is applied to characterize exponential decay constants (β) of the squared electronic coupling matrix element (V_{DA}^2) in transient, solvent-separated radical ion pairs (RIP) composed of quinone anions and several cation radicals in aprotic liquid solutions of N,N-dimethylformamide, DMSO, and benzonitrile. The distance dependence of singlet-triplet energy splitting ($2J$) is shown to be described by β in V_{DA} for charge-recombination processes. We show that the radical pair mechanism (RPM) electron spin polarization (P_{RPM}) is quite sensitive to β. The β value is characterized by using the stochastic Liouville equation to fit the experimental P_{RPM} values. The β values (from 0.8 to 1.0 Å^{-1}) manifest that V_{DA} is governed by the superexchange mechanism mediated by the intervening solvent molecules from a result that the β increases with increasing the tunneling energy gap (ΔG_{eff}) for solvent oxidation or reduction in several intermolecular electron-transfer systems. We propose a simple three-dimensional model of V_{DA}, in which the through-solvent tunneling pathways are exponentially increased with the increase in the intermolecular distance in bulk, condensed media. This model explains the ΔG_{eff} dependence of β, including the data previously reported on the charge-transfer reactions both in liquid and frozen (77 K) solutions. Effective solvent-solvent coupling is estimated to be $v_B \approx 850$ cm^{-1} at a mean nearest-neighbor distance of 5.7 Å. This relatively large magnitude of v_B may agree with dynamical amplifications of the effective coupling by low-frequency motions of the mediators as reported in charge-transfer reactions in biological systems. (Balabin, I. A. and Onuchic, J. *Science* **290**, 114 (2000) and Troisi, A. and Orlandi, G. *J. Phys. Chem. B* **106**, 2093 (2002).)

I-M Solvation Thermodynamics of Protein and Related Molecules

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

solvent. It is an extremely difficult problem by any means due to the overwhelmingly large degrees of freedom to be handled, including protein and solvent. 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 $V/N = const.$) 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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1-M-1 Solvation Thermodynamics of Protein Studied by the 3D-RISM Theory

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The partial molar volume and the solvation free energy of five globular proteins in aqueous solutions are calculated by the three-dimensional reference inter-action site model (3D-RISM) theory, a modern integral equation theory of molecular liquids.

The partial molar volume calculated by the theory shows quantitative agreement with the corresponding experimental data. Concerning the solvation free energy, the theoretical results are compared with estimations by an empirical method which uses the accessible surface area of atoms, because the corresponding experimental data are not available.

Possible applications of the method to problems related to the solvation thermodynamics of protein are discussed.

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

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

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

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I-N-1 A Mode-Coupling Analysis of the Translational and Rotational Diffusion of Polar Liquids; Acetonitrile and Water

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The translational and rotational motions of two representative polar liquids, water and acetonitrile, are investigated by the mode-coupling theory for molecular liquids based on the interaction-site model. The diffusive motion of acetonitrile agrees fairly well with that from the molecular-dynamics simulation. The pressure dependence of the translational and rotational diffusion coefficients is also in qualitative agreement with experiments. However, the reorientational relaxation of water is predicted to be much faster than that from experiments or simulations. The agreement between the theory and the simulation is partly improved by using the dynamic structure factor determined by the simulation. The effect of three-site correlation in the mode-coupling expression of the memory function is also examined.

I-N-2 Pressure Dependence of Diffusion Coefficient and Orientational Relaxation Time for Acetonitrile and Methanol in Water: DRISM/Mode-Coupling Study

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We present results of theoretical description and numerical calculation of the dynamics of molecular liquids based on the Reference Interaction Site Model/Mode-Coupling Theory. They include the temperature-pressure (density) dependence of the translational diffusion coefficients and orientational relaxation times for acetonitrile and methanol in water at infinite dilution. Anomalous behavior, *i.e.* the increase in mobility with density, is observed for the orientational relaxation time of methanol, while acetonitrile does not show any deviations from the usual. This efect is in qualitative agreement with the recent data of MD simulation and with experimental measurements, which tells us that presented theory is a good candidate to explain such kind of anomalies from the microscopical point of view and with the connection to the structure of the molecules.

I-O Statistical Mechanics of Interfacial Fluids

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

I-O-1 Molecular Description of Electrolyte Solution in a Carbon Aerogel Electrode

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We develop a molecular theory of aqueous electrolyte solution sorbed in a nanoporous carbon aerogel electrode, based on the replica reference interaction site model (replica RISM) for realistic molecular quenched-annealed systems. We also briefly review applications of carbon aerogels for supercapacitor and electrochemical separation devices, as well as theoretical and computer modelling of disordered porous materials. The replica RISM integral equation theory yields the microscopic properties of the electrochemical double layer formed at the surface of carbon aerogel nanopores, with due account of chemical specificities of both sorbed electrolyte and carbon aerogel material. The theory allows for spatial disorder of aerogel pores in the range from micro- to macroscopic size scale. We considered ambient aqueous solution of 1 M sodium chloride sorbed in two model nanoporous carbon aerogels with carbon nanoparticles either arranged into branched chains or randomly distributed. The long-range correlations of the carbon aerogel nanostructure substantially affect the properties of the electrochemical double layer formed by the solution sorbed in nanopores.

I-O-2 Microscopic Description of a Liquid-Vapor Interface by an Inhomogeneous Integral Equation Theory

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

We developed an inhomogeneous integral equation theory yielding the inhomogeneous pair correlation functions as well as the density profiles of the liquid-vapor interface of simple fluid. We analytically derived the long-range asymptotics of the inhomogeneous pair distribution along the interface, related to capillary waves. We showed that their physical nature is the same as long-range fluctuations of critical fluid which are restricted to the two-dimensional interfacial region by the external field shaping the interface.