

I-N 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.

$$V_{\lambda\lambda} = \sum_j \int \int \int \frac{q_j}{r} g_{j\lambda}(r) \psi_j(r)$$

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,

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

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

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

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

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

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I-N-1 Enthalpy and Entropy Decomposition of Free-Energy Changes for Side-Chain Conformations of Aspartic Acid and Asparagine in Acidic, Neutral, and Basic Aqueous Solutions

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Trans and gauche conformational equilibria in the side chains of aspartic acid (Asp) and asparagine (Asn) were investigated by measuring the vicinal spin-spin coupling constants of ¹H NMR in acidic, neutral, and basic aqueous solutions over a wide range of temperature (5–90 °C). The standard free-energy changes ΔG^0 were obtained for the trans to gauche conformational variations on the C_α–C_β bond with respect to the α-carboxyl group and the β-carboxyl group in Asp (β-amide in Asn) and were decomposed

into enthalpic ΔH^0 and entropic- $T\Delta S^0$ components. The hydration of ionic and polar groups in Asp competes against the large intramolecular electrostatic repulsion energy and stabilizes the gauche more than the trans conformer in correspondence to a larger degree of separation of positive and negative partial charges. In the neutral solutions, where both the carboxyl groups are negatively ionized, the hydration part even overwhelms the intramolecular repulsion and leads to a negative ΔH^0 . The fact that the hydration almost cancels the intramolecular electrostatic repulsion contradicts the widely accepted view that the trans preference in the conformational equilibrium is due to the intramolecular repulsion between α-CO₂⁻ and β-CO₂⁻ (or β-CONH₂).

I-N-2 Theoretical Study on Electronic and Solvent Reorganization Processes Associated with a Charging Process of Organic Compounds: I. Molecular and Atomic Level Description of Solvent Reorganization

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[*J. Chem. Phys.* **119**, 2753 (2003)]

Electronic and solvation structures of *N,N*-dimethylaniline (DMA) in acetonitrile are examined by means of the ab initio reference interaction site model—self-consistent field (RISM-SCF) theory coupled with the method to evaluate nonequilibrium solvation free energy developed by Chong *et al.* [*J. Phys. Chem.* **99**, 10526 (1995)]. The key quantities characterizing the solvation process, free energy profile governing the solvent fluctuations and solvent reorganization, are evaluated from the first principle. A new scheme, which enables us to partition solvent reorganization into atomic contributions in the solute molecule, is proposed and used to analyze the process in atomic level. We found that the linear response approximation holds well and the overall observable, λ_s is not much affected by solute geometry, while the individual atomic contribution is significantly changed, especially, by the wagging motion of the amino group.

I-N-3 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-N-4 Interplay between the Repulsive and Attractive Interaction and the Spatial Dimensionality of an Excess Electron in a Simple Fluid

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The behavior of an excess electron in a one, two and three dimensional classical liquid has been studied with the aid of Chandler, Singh and Richardson (CSR) theory [*J. Chem. Phys.* **81**, 1975 (1984)]. The size or dispersion of the wavepacket associated with the solvated electron is very sensitive to the interaction between the electron and fluid atoms, and exhibits complicated behavior in its density dependence. The behavior is interpreted in terms of an interplay among four causes: the excluded volume effect due to solvent, the pair attractive interaction between the electron and a solvent atom, the thermal wavelength of the electron (λ_e), a balance of the attractive interactions from different solvent atoms and the range of repulsive interaction between electron and solvent atom. Electron self-trapping behavior in all the dimensions has been studied for the same solvent-solvent and electron-solvent interaction potential and the results are presented for the same parameter in every dimension to show the comparison between the various dimensions.

I-O Solvation Thermodynamics of Protein and Related Molecules

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

candidate of such methods, which provides not only solvation thermodynamics but also microscopic description at the level of the pair correlation functions.¹⁾ Obvious technical difficulties which one may face in applying the theory to such a large system are not only the computation time but also the stability of the numerical solution.²⁾

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

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1-O-1 Partial Molar Volume and Compressibility of a Molecule with Internal Degrees of Freedom

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Statistical mechanical expressions for the partial molar volume (PMV) and the partial molar compressibility (PMC) of a solute molecule with internal degrees of freedom are derived. The equilibrium PMV is expressed simply by the conformational ensemble average of PMV. The equilibrium PMC consists of two terms: the conformational ensemble average of PMC and the mean square fluctuation of PMV along conformational axis. As an illustrative application of the theory, the equilibrium PMV and PMC of butane in aqueous solution are calculated from the relations, in which the thermodynamic quantities of each conformer appearing in the relations are obtained by the RISM theory. The conformational ensemble average of PMC is the predominant contribution to the equilibrium PMC in this particular example. Possibility of shedding light on the protein conformation in terms of PMV and PMC is discussed.

1-O-2 A Density-Functional Theory for Polymer Liquids Based on Interaction Site Model

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[*J. Chem. Phys.* **118**, 2431 (2003)]

The density-functional theory (DFT) for molecular fluids [*J. Chem. Phys.* **115**, 6653 (2001)] is extended to the case of polymer liquids. A system consisting of the ideal chains is employed as a reference system for the DFT, where many-body effects are considered as an effective field that acts on each site of the ideal chains. We derived a relation between the site-site pair distribution functions and the site-density distribution functions under a mean field arising from a single polymer molecule. An integral equation for the site-site pair distribution functions is obtained by the DFT, where the external field is taken to be the mean field. We propose an approximate expression of the intramolecular correlation functions for isolated single-polymer chains to take account for the excluded volume effects inside a polymer chain. The intramolecular correlation function considering the excluded volume effects was in qualitative agreement with those obtained from a simulation for liquid consisting of freely jointed tangent-soft-core chains. The site-density integral equation under the mean field, using the intramolecular correlation function, reproduces the simulation results for site-site pair distribution functions of the system of freely jointed tangent-soft-core chains.

I-P 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-P-1 Solute-Structure Dependence of Solvation Dynamics Studied by Reference Interaction-Site Model Theory

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[*J. Chem. Phys.* **118**, 2279 (2003)]

A combination of the reference interaction-site model theory and site-site Smoluchowski-Vlasov equation is applied to estimate the dynamic response function of the average-energy relaxation of the solute-solvent system, $S_S(t)$. We calculate $S_S(t)$ for 13 model solutes with different structure, from a simple ion to an octopole, in a polar solvent. The partial charges of the ions and multipoles are changed to investigate nonlinear character of $S_S(t)$. The "nonlinear character" we study here corresponds to the response of the solvent fluctuation after the sudden change of the solute charge-distribution. Our present results reveal that $S_S(t)$ depends on the molecular structure and charge distribution of the solute. $S_S(t)$ is decomposed into two parts: one corresponding to the optical mode of solvent, the other to the acoustic mode. We show that for multipoles the optical mode is responsible for the fast part of $S_S(t)$, while the acoustic mode plays an important role in the slower dynamics. The dual nature of $S_S(t)$ is essential for the nonlinearity of solvation dynamics.

I-P-2 Dielectric Relaxation Spectrum of Water Studied by the Site-Site Generalized Langevin/Modified Mode-Coupling Theory

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The dielectric relaxation spectrum of water is calculated from the site-site generalized Langevin/modified mode-coupling theory. The main part of the relaxation follows the Debye-type function, and a small deviation from the Debye relaxation is found on the high-frequency side. This tendency is consistent with recent experiments, although the absolute relaxation time does not agree with the experimental value quantitatively. The time-development of the longitudinal polarization function resembles the dielectric part of the

memory function, and we consider that this is because the dielectric friction dominates the collective reorientation of the dipole moment of water. We performed calculations with different dielectric constants using the reference interaction-site model integral equation, and found that the large gap between the time-scales of the dielectric relaxation and the longitudinal polarization relaxation causes the Debye-type dielectric relaxation when the dielectric friction is dominant in the friction on the collective reorientation of the dipole moment. Namely, the longitudinal polarization relaxation is fast enough to be considered as a white noise to the dielectric relaxation process, so that the relaxation becomes a Markov process. The large gap between the two relaxation times originates from a large local field correction due to the large dielectric constant of water. It is also suggested that the deviation from the Debye relaxation at the high-frequency side is the manifestation of the slow memory caused by the long-time part of the longitudinal polarization relaxation in the low-wavenumber region.

I-P-3 Theoretical Study on the Molecular Motion of Liquid Water under High Pressure

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The pressure effects on the molecular dynamics of liquid water are investigated using the site-site generalized Langevin/modified mode-coupling theory. The calculations are performed for temperatures from 273 to 373 K and densities from 0.9 to 1.2 g/cm³. The static structure factor required as input is obtained from the reference interaction-site model/hypernetted chain integral equation. The shear viscosity, the dielectric relaxation time, the translational diffusion coefficient, and the first-rank reorientational relaxation times are evaluated. All these quantities show unusual pressure dependence in the low-density, low-temperature region in that the molecular mobility is enhanced by applying the pressure. The magnitude of the enhancement is larger on the reorientational motions than on the translational ones. These tendencies are consistent with experimental observations, although the quantitative agreement is not so good. An analysis of the theory indicates that the decrease in the dielectric friction on the collective polarization at small wavenumbers upon

increasing pressure is the principal reason for the pressure-induced enhancement of the dielectric relaxation, and the decrease in the dielectric relaxation time affects other motions. The decrease in the dielectric friction is caused by the decrease in the number-density fluctuation around the low-wavenumber edge of the first-peak of the structure factor by compression. The comparison between the results for water and acetonitrile extracts two characteristic features of water that are important for the anomalous pressure effect on its molecular motion. The first one is the small

collisional friction on the reorientation due to the spherical repulsive core, and the second one is the strong short-range Coulombic interaction caused by the formation of the hydrogen-bonding. A theoretical calculation on a model diatomic liquid consisting of oxygen and hydrogen atoms proposes that the above two characteristic properties of water are sufficient for the emergence of the anomalous pressure dependence. This conclusion is also supported by the molecular dynamics simulation performed on the same model diatomic liquid.

I-Q 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-Q-1 Compressibility of Tert-Butyl Alcohol-Water Mixture: The RISM Theory

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The isothermal compressibility χ_T of binary mixtures of water and *tert*-butyl alcohol (TBA) is calculated using the reference interaction site model (RISM) integral equation theory. The calculations are performed over the whole concentration from $x = 0$ to 1 and a wide temperature from $T = 283$ to 313 K ranges employing an extended point charge model for water and optimized site-site potentials for TBA molecules. The results obtained are compared versus available experimental data. It is demonstrated that, despite an approximate character of the model potentials and closure relation applied, the theory is able to reproduce qualitatively all main features of the x - and T -dependencies of χ_T inherent in real experiment. Such features include the decrease of compressibility with increasing T in the low TBA concentration limit $x \rightarrow 0$ (pure water), and the increase of χ_T with rising T in the opposite regime $x \rightarrow 1$ (pure alcohol); the presence of a concentration region where the function $\chi_T(x, T)$ does not depend much on T ; as well as the existence of a minimum in χ_T with respect to x at each given T . The question of how to achieve a quantitative agreement between the theoretical and experimental values by correcting the closure relation is also discussed.

I-Q-2 Molecular Theory of an Electrochemical Double Layer in a Nanoporous Carbon Supercapacitor

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[*Chem. Phys. Lett.* **378**, 638 (2003)]

We develop the replica RISM theory of electrolyte solution sorbed in a nanoporous carbon electrode. The model comprises carbon nanospheres forming a disordered network with the porosity, pores sizes and surface area fitted to carbonized polyvinylidene chloride (PVDC) material, and to activated carbon. We obtained the huge capacitance comparable to that achieved in supercapacitors, and found the higher capacitance per pores surface for carbonized PVDC material with uniform nanoporous texture than for activated carbon with micro- as well as nanopores. Unlike a planar electrochemical double layer with the voltage dominated by the inner layer, the nanoporous supercapacitor voltage is driven by the solvation chemical potentials of the sorbed ions.