

## 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 referred to as RISM-SCF based on the integral equation theory of molecular liquids (RISM) and the *ab initio* electronic structure theory (SCF).<sup>1)</sup> 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  $\lambda$  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  $V_{\lambda}$  the solvated Fock operator is defined as,

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

where  $b_{\lambda}$  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.<sup>2)</sup> Defining the Helmholtz free energy  $A$  as following;

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

where  $E_{\text{solute}}$  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 The Syn-/Anti- Conformational Equilibrium of Acetic Acid in Water Studied by the RISM-SCF/MCSCF Method

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[*J. Mol. Struct. (THEOCHEM)* **461**, 113 (1999)]

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 is 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-N-2 RISM-SCF Study for the Free Energy Profile of Menshutkin Type Reaction $\text{NH}_3 + \text{CH}_3\text{Cl} \rightarrow \text{NH}_3\text{CH}_3^+ + \text{Cl}^-$ in Aqueous Solution

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[*Theor. Chem. Acc.* **102**, 165 (1999)]

The free energy profile for the Menshutkin type reaction  $\text{NH}_3 + \text{CH}_3\text{Cl} \rightarrow \text{NH}_3\text{CH}_3^+ + \text{Cl}^-$  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-N-3 Thermodynamic Analysis of the Solvent Effect on Tautomerization of Acetylacetone: An Ab Initio Approach

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[*J. Chem. Phys.* **110**, 3938 (1999)]

The keto-enol tautomerism of acetylacetone in solution is studied with the reference interaction site model self-consistent-field (RISM-SCF) method. We choose three solvents, H<sub>2</sub>O, dimethyl sulfoxide (DMSO), and carbon tetrachloride (CCl<sub>4</sub>), representing, respectively, protic polar, aprotic polar and nonpolar solvents. The analysis is made taking account of the solute electronic as well as geometrical change of the tautomers due to solvent effect. In addition, the electronic correlation energy of solute molecule and solute vibrational energies are considered. The free energy differences are analyzed by decomposing them into the enthalpy and entropy terms. The theory reproduces the total free energy determined by the experiment fairly well. We also find that, as solvent polarities increase, the keto tautomer shows the drastic geometric change in order to make its dipole moment larger and that the geometric change of the keto tautomer is enthalpically driven in H<sub>2</sub>O and entropically in DMSO. It is made clear that these depend on the solvent property protic or aprotic.

### I-N-4 Solvation Dynamics of Benzonitrile Excited State in Polar Solvents: A Time-Dependent Reference Interaction Site Model Self-Consistent Field Approach

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[*J. Chem. Phys.* **110**, 11423 (1999)]

The solvation dynamics of benzonitrile (C<sub>6</sub>H<sub>5</sub>CN) after the 2<sup>1</sup>A<sub>1</sub> ← 1<sup>1</sup>A<sub>1</sub> vertical transition in water (H<sub>2</sub>O), methanol (CH<sub>3</sub>OH), and acetonitrile (CH<sub>3</sub>CN) solvents is studied with the reference interaction site model self-consistent field (RISM-SCF) method. The evolution of solute electronic states associated with the solvent relaxation is described by a time-dependent RISM-SCF method, incorporating the time-dependent solute-solvent site-site radial distribution functions, which are derived from the surrogate linear response theory. Ab initio electronic structure calculations reveal that the 2<sup>1</sup>A<sub>1</sub> state is of ionic nature whose dipole moment is larger by 2.41 D than that of the ground state. It is found that the excited state dipole moment is enhanced in the solutions, which provides the red shift of ~6000 cm<sup>-1</sup> in the vertical excitation energy. The solvent relaxation further increases the charge polarization in solute, indicating the electronic state of excited

C<sub>6</sub>H<sub>5</sub>CN is sensitive to the electrostatic field coming from the solvent. The dynamic Stokes shift is characterized by the solvation time correlation function (STCF). The calculated STCFs show that the solvent relaxation exhibits a nonexponential behavior and almost completes within 5 ps in H<sub>2</sub>O and CH<sub>3</sub>CN while a long-time tail is observed up to 20 ps in CH<sub>3</sub>OH. The slow component of the decay rate is consistent with other simulation calculations though the fast one is smaller. In order to analyze the solute charge polarization during the solvent relaxation, the solute charge time correlation function (CTCF) is calculated and the resultant CTCFs are discussed in terms of the solvent charge polarization in the vicinity of solute molecule.

### I-N-5 Revisiting the Acid-Base Equilibrium in Aqueous Solutions of Hydrogen Halides: Study by the ab Initio Electronic Structure Theory Combined with the Statistical Mechanics of Molecular Liquids

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[*J. Am. Chem. Soc.* **121**, 2460 (1999)]

The classical problem of acid strength of the hydrogen halides in aqueous solution is revisited by means of the RISM-SCF/MCSCF theory, an ab initio electronic structure theory combined with the statistical mechanics of molecular liquids. Free energy changes associated with the chemical equilibrium HX + H<sub>2</sub>O → X<sup>-</sup> + H<sub>3</sub>O<sup>+</sup> are studied for a series of hydrogen halides (X: F, Cl, Br, I). The free energy differences between hydrogen halides and the dissociated anions are mainly governed by the subtle balance of the two energetic components—formation energies of hydrogen halides and solvation energies of the anions. It is shown that hydration structure around hydrogen fluoride is qualitatively different from the other three hydrogen halides. The well-known specificity of the hydrogen fluoride with respect to the acidity in aqueous solution is explained in terms of the characteristic hydration structure. Molecular geometries and electronic structures of the solute molecule as well as the solvation structure and free energy components are also discussed in detail. The old concept of electronegativity proposed by Pauling is reexamined on the basis of the modern theoretical approach.

### I-N-6 Ab Initio Study on Molecular and Thermodynamic Properties of Water: A Theoretical Prediction of pK<sub>w</sub> over a Wide Range of Temperature and Density

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[*J. Phys. Chem. B* **103**, 6596 (1999)]

The ionic product of water (pK<sub>w</sub>) has been calculated in a wide range of temperature (0–600 °C) and density (0.6–1.4 g/cm<sup>3</sup>) by means of ab initio electronic structure theory combined with the extended reference interaction site model in statistical mechanics for molecular liquids (RISM-SCF/MCSCF). We

consider the autoionization process ( $\text{H}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}^-$ ) by regarding  $\text{H}_2\text{O}$ ,  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  as "solute" molecules in an aqueous solution and evaluate molecular geometries, electronic structure, solvation structure, and free energy components of these species as functions of thermodynamical conditions. The results for  $\text{p}K_w$  obtained from the theory have shown a monotonical decrease with increasing density at all the temperatures investigated, in good accord with the experimental observation. The behavior is determined essentially by

the difference in solvation free energies,  $\Delta\mu(\text{H}_3\text{O}^+) + \Delta\mu(\text{OH}^-) - 2\Delta\mu(\text{H}_2\text{O})$ , associated with the reaction. The  $\Delta\mu(\text{OH}^-)$  shows the density dependence, which is entirely different from that of the other species and which gives rise to the observed behavior for  $\Delta\log K_w$ . It is shown through analyses of the electronic structure of the "solutes" that the distinct density dependence of  $\Delta\mu(\text{OH}^-)$  has the origin in its rather "soft" electronic cloud interacting with solvent polarization.

## 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.<sup>1)</sup> 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.<sup>2)</sup>

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).<sup>3)</sup> 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-O-1 Calculation of Solvation Free Energy for Peptide in Salt Solution Using the RISM Theory

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[*J. Comput. Chem.* **19**, 1724 (1998)]

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 ( $\text{NH}_2\text{-CHCH}_3\text{-CONH-CHCH}_3\text{-COOH}$ ) 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-O-2 Singular Behavior of the RISM Theory Observed for Peptide in Salt Solution

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[*Chem. Phys. Lett.* **297**, 433 (1998)]

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-O-3 Analysis on Conformational Stability of C-Peptide of Ribonuclease A in Water Using the Reference Interaction Site Model Theory and Monte Carlo Simulated Annealing**

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[*J. Chem. Phys.* **110**, 4090 (1999)]

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<sup>+</sup>, Glu-2<sup>-</sup>, Lys-7<sup>+</sup>, Arg-10<sup>+</sup>, and His-12<sup>+</sup> (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-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).<sup>1</sup> 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.<sup>2</sup> 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.<sup>3</sup>

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 Effect of Molecular Symmetry on Electrical Potential Fluctuations of Solvent around Solute in Polar Liquid**

**CHONG, Song-Ho<sup>1</sup>; HIRATA, Fumio**  
(<sup>1</sup>Kyoto Univ.)

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

The electrical potential fluctuations of solvent around solute in polar liquid are studied using the recently developed method based on an integral equation theory of molecular liquids. We focus on how the molecular symmetry of 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.

**I-P-2 Mode-Coupling Theory for Molecular Liquids Based on the Interaction-Site Model****CHONG, Song-Ho<sup>1</sup>; HIRATA, Fumio**  
(<sup>1</sup>Kyoto Univ.)[*Phys. Rev. E* **58**, 6188 (1998)]

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-P-3 Time-Correlation Functions in Molecular Liquids Studied by the Mode-Coupling Theory Based on the Interaction-Site Model****CHONG, Song-Ho<sup>1</sup>; HIRATA, Fumio**  
(<sup>1</sup>Kyoto Univ.)[*Phys. Rev. E* **58**, 7296 (1998)]

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-P-4 Dynamics of Ions in Liquid Water: An Interaction-Site-Model Description****CHONG, Song-Ho<sup>1</sup>; HIRATA, Fumio**  
(<sup>1</sup>Kyoto Univ.)[*J. Chem. Phys.* **111**, 3654 (1999)]

We present a molecular theory for investigating the dynamics of ions in polar liquids. The theory is based on the interaction-site model for molecular liquids and on the generalized Langevin equation combined with the mode-coupling theory. The velocity autocorrelation function, diffusion and friction coefficients of ions in water at 25 °C and at infinite dilution are studied. The theoretical results for the velocity autocorrelation functions exhibit a gradual change from oscillatory to monotonic decay as the ion size increases. The diffusion (friction) coefficients of ions in aqueous solutions pass through a maximum (minimum) as a function of the ion size, with distinct curves and maxima (minima) for

positive and negative ions. These trends are in complete accord with those of the molecular dynamics simulation results performed on the same system by Rasaiah and co-workers [*J. Phys. Chem. B* **102**, 4193 (1998)]. It is worthwhile to mention that this is the first molecular theory that is capable of describing the difference in the dynamics of positive and negative ions in aqueous solutions. A further analysis of the friction coefficients of ions in water is presented in which the friction is decomposed into the “Stokes,” dielectric and their cross terms. The Stokes and dielectric terms arise from the coupling of the ion dynamics to essentially the acoustic dynamics of the solvent via the short-range interaction, and from the coupling to the optical mode of the solvent via the long-range interaction. The most striking feature of our results is that the Stokes friction so defined does not increase monotonically with increasing ion size, but decreases when ions are very small, implying a formation of a molecular “complex” comprising the ion and its nearest neighbor solvent molecules. Interesting observations concerning the cross term are: (1) its magnitude is rather large for small ions and cannot be neglected at all, and (2) the cross term for small ions seems to cancel out the Stokes part, and consequently the total friction for small ions seems to be to a large extent determined by its dielectric component.

**I-P-5 Interaction-Site-Model Description of Collective Excitations in Liquid Water. I: Theoretical Study****CHONG, Song-Ho<sup>1</sup>; HIRATA, Fumio**  
(<sup>1</sup>Kyoto Univ.)[*J. Chem. Phys.* **111**, 3083 (1999)]

Collective excitations in liquid water are investigated using the recently developed 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 simple approximation scheme for memory functions. It is shown that all the essential features of collective excitations in water, reported previously by neutron-scattering experiments, molecular dynamics simulations and dielectric theories, are well reproduced by the present theory.

**I-P-6 Interaction-Site-Model Description of Collective Excitations in Liquid Water. II: Comparison with Simulation Results****CHONG, Song-Ho<sup>1</sup>; HIRATA, Fumio**  
(<sup>1</sup>Kyoto Univ.)[*J. Chem. Phys.* **111**, 3095 (1999)]

Theoretical results for dynamical correlation functions characterizing collective excitations in liquid water reported in a previous paper are compared with molecular dynamics simulation results performed on the same system. We also examine the validity and accuracy of the approximation scheme for memory functions employed in our theory by investigating

whether the assumed form for memory functions and resulting expressions for dynamical correlation functions can be used as faithful models to reproduce the "experimental" data determined from the simulation.

### I-P-7 Solvation Dynamics of a Quadrupolar Solute in Dipolar Liquids

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[*J. Phys. Soc. Jpn.* **68**, 303 (1999)]

A microscopic calculation of solvation dynamics of dipolar and quadrupolar solutes in liquid water and acetonitrile is presented. The solvation is found to be biphasic. The calculated solvation time correlation function of ionic quadrupolar solute ( $K^+$ ) in water is in good agreement with recent computer simulation results. Present study reveals some interesting aspects of quadrupolar solvation dynamics which differ significantly from that of ionic and dipolar solvation.

### I-P-8 Density Matrix for an Excess Electron in a Classical Fluid: Results for a One-Dimensional System

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[*J. Chem. Phys.* **110**, 10086 (1999)]

We extend the theory of Chandler, Singh, and Richardson [*J. Chem. Phys.* **81**, 1975 (1984)] to calculate the density matrix for an excess electron in a classical liquid like bath. For a one-dimensional fluid of hard rods and for two model potentials representing the

electron fluid atom interaction (one representing the excluded volume effect and the other attractive interaction), we calculate the density matrix using the values of solvent induced potential surfaces for the electron found from our earlier calculations [*Phys. Rev. B* **42**, 6090 (1990)]. The resulting density matrix is diagonalized and values of energies and wave-functions of the electron including the effective mass and root mean square (RMS) displacement  $R_\beta$  in imaginary time  $\beta\hbar/2\pi$ . The transition of the electron to a state of self-trapping is visualized through a sudden change in the value of  $R_\beta$  or the effective mass  $m^*$  at a value of  $\beta$  or solvent density  $\rho^*$ . For a potential model of hard rods, we find that the RMS displacement  $R_\beta$  for a given solvent density varies as  $(\beta\hbar/2\pi)^\nu$ . Values of  $\nu$  are evaluated for several solvent densities.

### I-P-9 Polaron Density Matrix and Effective Mass at Finite Temperature

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[*Phys. Rev. B* **60**, 7245 (1999)]

We calculate the density matrix elements of the polaron using the Feynman's variational method. The density matrix is diagonalized and the eigenvalues and eigenfunctions are derived. These results and the calculated density matrix are used to evaluate the root mean square (RMS) displacements  $R_\beta$  and the effective mass (EM)  $m^*$  for various values of coupling strengths between electron and medium and the temperature. We find that EM is related to the RMS displacement. The temperature dependence of EM is in qualitative agreement with experiment.

## I-Q Liquid-Solid Interface

Due to recent progress in experimental techniques in the in situ measurements, the electrochemistry seems making a new epoch in understanding the chemical processes at electrode-solution interfaces. For examples, the scanning tunneling microscope (STM) applied to the interface has been revealing detailed atomic structure of the interface.<sup>1)</sup> The surface enhanced infrared absorption spectroscopy has provided detailed picture regarding the orientation of water molecules at the surface.<sup>2)</sup> 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.<sup>3)</sup> 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 method 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-Q-1 Acceleration of Liquid Structure Calculations by Modified Direct Inversion in the Iterative Subspace

KOVALENKO, Andriy F.; TEN-NO, Seiichiro; HIRATA, Fumio

[*J. Comput. Chem.* **20**, 928 (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-Q-2 Extended States of a Shallow Donor Located Near a Semiconductor-Insulator Interface

KOVALENKO, Andriy F.

[*Int. J. Quantum Chem.* **66**, 435 (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-Q-3 Free Energy Profiles of Electron Transfer at Water-Electrode Interface Studied by the Reference Interaction Site Model Theory

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[*Chem. Phys. Lett.* **305**, 251 (1999)]

Free energy profiles governing electron transfer from a reactant to an electrode surface in water are investigated, based on the reference interaction site model (RISM) theory. Three models of a redox pair for charge separation reactions are examined: a pair of atomic solutes, and systems consisting of an atom and a surface with a localized or a delocalized electron. The profile becomes highly asymmetrical, when an electron in the electrode is delocalized. The behaviors are essentially due to the asymmetrical response of water polarization to positive and negative charges of solute. The results are related to models of ion-hydration.

### I-Q-4 Self-Consistent Description of a Metal-Water Interface by the Kohn-Sham Density Functional Theory and the Three-Dimensional Reference Interaction Site Model

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[*J. Chem. Phys.* **110**, 10095 (1999)]

We have developed a self-consistent description of an interface between a metal and a molecular liquid by a combination of the density functional theory in the Kohn-Sham formulation (KS DFT) for the electronic structure, and the three-dimensional generalization of the reference interaction site model (3D RISM) for the classical site distribution profiles of liquid. The electron and classical subsystems are coupled in the mean field approximation. The procedure takes account of many-body effects of dense fluid on the metal-liquid interactions by averaging the pseudopotentials of liquid molecules over the classical distributions of the liquid. The proposed approach is substantially less time-consuming as compared to a Car-Parrinello-type simulation since it replaces molecular dynamics with the integral equation theory of molecular liquids. The calculation has been performed for pure water at normal conditions in contact with the (100) face cubic centered (fcc) surface of a metal roughly modeled after copper. The results are in good agreement with the Car-Parrinello simulation for the same metal model. The shift of the Fermi level due to the presence of water conforms with experiment. The electron distribution near an adsorbed water molecule is affected by dense water, and so the metal-water attraction follows the shapes of the metal effective electrostatic potential. For the metal model employed, it is strongest at the hollow

site adsorption positions, and water molecules are adsorbed mainly at the hollow and bridge site positions rather than over metal atoms. Layering of water molecules near the metal surface is found. In the first hydration layer, adsorbed water molecules are oriented in parallel to the surface or tilted with hydrogens mainly outwards the metal. This orientation at the potential of zero charge agrees with experiment.

### **I-Q-5 Effective Interaction between Hard Sphere Colloidal Particles in a Polymerizing Yukawa Solvent**

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[*J. Chem. Phys.* **110**, 8189 (1999)]

The effective interaction between colloidal hard sphere particles in a Yukawa solvent that can polymerize with the formation of chains and rings is studied and compared with the corresponding results for colloidal hard sphere particles in a solvent of polymerizing hard spheres. The attractive nature of the polymerizing Yukawa solvent particles induces significant changes in the effective interactions between the colloid particles as compared to a polymerizing solvent of hard spheres that was investigated in previous studies. The results for the colloid-solvent mixture are obtained using the associative Percus-Yevick approximation for Wertheim's Ornstein-Zernike integral equation; the colloidal species are taken at a non-vanishing but very small concentration throughout this article. We present the effects of the size ratio of colloid spheres to solvent spheres, the degree of polymerization, and the solvent density on the effective interactions between colloid and solvent particles. The intercolloidal potential of mean force (PMF) is found to be highly dependent on these parameters for Wertheim's model. It is found that the correlations between colloid particles obtained using the Yukawa solvent model are longer ranged and more attractive than those found using the hard sphere solvent model. A greater depletion of the solvent density around the colloidal particles is also observed for the Yukawa solvent model as compared to the hard sphere model; an increased polymer chain length also enhances the depletion of the solvent density. The PMF is found to be oscillatory in structure. The oscillatory structure also depends upon the average polymer chain length, specifically, the oscillatory structure in the PMF is strongly diminished as the average polymer chain length increases. Additionally, as the average polymer length increases, the attraction at the colloid-colloid contact distance decreases.

### **I-Q-6 Potential of Mean Force between Two Molecular Ions in a Polar Molecular Solvent: A Study by the Three-Dimensional Reference Interaction Site Model**

**KOVALENKO, Andriy F.; HIRATA, Fumio**

[*J. Phys. Chem. B* **103**, 7942 (1999)]

The orientationally dependent potential of mean force (PMF) between two charged polyatomic solutes immersed in a polar molecular solvent is obtained by using the three-dimensional reference interaction site model (3D RISM) of the integral equation theory. We propose the partially linearized hypernetted chain (PLHNC) closure. The method is applied to the *N,N*-dimethylaniline cation (DMA<sup>+</sup>) and the anthracene anion (AN<sup>-</sup>) in acetonitrile solvent (CH<sub>3</sub>CN). We solve the 3D RISM integral equations by employing the modified direct inversion in the iterative subspace (MDIIS) method. The 3D site distributions of solvent around each solute are obtained and discussed. The PMF between the solutes is calculated as a 3D profile dependent on the relative position of the solutes at six characteristic relative orientations. The PMF obtained is in qualitative agreement with the results of molecular dynamics simulations. In solvent, the AN<sup>-</sup> solute effectively attracts the DMA<sup>+</sup> dimethylamino group and repels its phenyl ring. We found that the most stable relative arrangement of the DMA<sup>+</sup> and AN<sup>-</sup> molecules in acetonitrile solvent is different from that in gas phase.

### **I-Q-7 Self-Consistent, Kohn-Sham DFT and Three-Dimensional RISM Description of a Metal-Molecular Liquid Interface**

**KOVALENKO, Andriy F.; HIRATA, Fumio**

[*J. Mol. Liq.* submitted]

We have developed a self-consistent description of a metal-molecular liquid interface by combination of the Kohn-Sham density functional theory (KS DFT) for the electronic density, and the three-dimensional reference interaction site model (3D RISM) integral equation theory for the classical site distribution profiles of molecular liquid. The electron and classical subsystems are coupled in the mean field approximation. The classical potentials of the metal acting on species of the liquid are taken in the linear response regime. Many-body effects of dense liquid on metal valence electrons are allowed for by averaging pseudopotentials of liquid molecules over the site distributions of liquid. The coupled KS DFT and 3D RISM equations are solved simultaneously by using the procedure of dynamic relaxation. The proposed approach is substantially less time-consuming as compared to a Car-Parrinello type simulation. A partial linearization of the hypernetted chain (PLHNC) closure to the RISM equation is proposed. The calculation is performed in the supercell technique for water at normal conditions in contact with the (100) FCC slab of a metal roughly modeled after copper. The results are in good agreement with the Car-Parrinello simulation for the same model. Further applications of the method proposed are discussed.