

I-R Electronic Structure of a Molecule in Solution

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

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

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

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

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

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

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

where E_{solute} is the energy of solute under solvent influence, and Δu 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-R-1 Ab initio Study of Water: Liquid Structure, Electronic and Thermodynamic Properties over a Wide Range of Temperature and Density

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[*J. Chem. Phys.* **111**, 8545 (1999)]

The electronic and liquid structures of water and its thermodynamic properties are studied over a wide range of temperature (0°–600 °C) and density (0.6–1.4 g/cm³) based on the ab initio molecular orbital theory combined with the integral equation method of liquid. Unlike standard treatments of water by means of the classical statistical mechanics including molecular simulations, the effective charges on oxygen and hydrogen atoms in water molecules are not “input parameters,” but naturally predicted from the theory in the course of self-consistent determination of the electronic structure and the density pair correlation functions in liquids. It is found that the molecular dipole moments and electronic polarization energies decrease with increasing temperature and/or density. The theoretical results for dipole moments are in quantitative accord with the experimental data, which has been determined based on

the NMR chemical shift coupled with the molecular dynamics simulation. The state dependence of the electronic structure is discussed in terms of the thermal activation of molecules and intermolecular interactions including the hydrogen bonds. The liquid structure of water is discussed in the wide range of thermodynamic states in terms of $S(r)$, an average response of the pair correlation functions to temperature change which is introduced in the present study in order to make structural characteristics of water more distinctive. It is concluded from the behavior of the function that the short range structure of water retains the characteristics to ice, or the tetrahedral configuration, over relatively wide range of temperature in the normal density (1.0 g/cm³). The ice-like characteristics of water disappear to large extent both at high (1.4 g/cm³) and low (0.6 g/cm³) densities for different reasons: in the high density due to the packing effect, while in the low density due to essentially entropic cause, or increased configuration space available to a molecule. The distance between the nearest-neighbor molecules in water are insensitive to the density change compared with those corresponding to the Lennard-Jones fluid. The difference in the behaviors between the two fluids is explained in terms of the intermolecular interactions and liquid structures. The number of hydrogen bonds is

calculated from the oxygen–hydrogen pair correlation function using a new definition based on $S(r)$, which enables us to distinguish the hydrogen-bonded OH pairs from those just in contact due to packing effect. The temperature and density dependence of the quantity is discussed in terms of the liquid structure of water.

I-R-2 Solvent Effects on a Diels-Alder Reaction in Supercritical Water: RISM-SCF Study

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[*J. Am. Chem. Soc.* **122**, 2289 (2000)]

A Diels-Alder reaction in supercritical water is studied by means of combined electronic structure and liquid state theories. The target system is the cycloaddition of cyclopentadiene with methyl vinyl ketone. The rate and the yield of the reaction in supercritical water are calculated and compared with those in ambient water. The activation free energies of the two isomers, *cis* and *trans*, are compared. The results are in agreement with the experimentally observed increase of the rate and the yield. The solvation effect for the rate constant is decreased in supercritical water, but the rate is increased because of the thermal excitation rather than the solvation effect. The *trans*-conformer has shown less activation energy in ambient water and supercritical water compared to the *cis*-conformer. The estimated yield in supercritical water is more than 600 times higher than in ambient water. The high yield in supercritical water is due to the high solubility of the reactants to supercritical water.

I-R-3 A Theoretical Study on a Diels-Alder Reaction in Ambient and Supercritical Water: Viewing Solvent Effects through Frontier Orbitals

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[*Chem. Phys.* **258**, 151 (2000)]

Solvent effects on the *endo/exo* selectivity of an asymmetric Diels-Alder reaction in ambient and supercritical water are studied by means of a combined electronic structure and liquid state theory. The target system is the cycloaddition of cyclopentadiene with methyl vinyl ketone. The rate constant and the equilibrium constant are obtained from the activation free energies and the free energy change of reaction for the two isomers. The results for the equilibrium constant are in qualitative agreement with the experimentally observed *endo/exo* selectivity. The relative rate constants show that the *endo* reaction occurs preferentially in wide range of thermodynamic conditions. Difference of the solvation free energy shows that *endo/exo* selectivity is enlarged in ambient water by hydrophobic effect and that it disappears completely in supercritical water.

The theoretical results are analyzed in the light of the frontier orbital theory in order to acquire physical insight of solvent effects on the stereo-selectivity.

I-R-4 Self-Consistent Field, *Ab initio* Molecular Orbital and Three-Dimensional Reference Interaction Site Model Study for Solvation Effect on Carbon Monoxide in Aqueous Solution

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[*J. Chem. Phys.* **112**, 9463 (2000)]

We have developed a three-dimensional (3D) extension of the reference interaction site model-self-consistent field (RISM-SCF) method to treat the electronic structure of a solvated molecule. The site-site treatment of the solute-solvent correlations involving the approximation of radial averaging constitutes a bottleneck of the RISM-SCF method, and thus lacks a 3D picture of the solvation structure for complex solutes. To resolve this problem, we devised out a 3D generalization of the RISM integral equations which yields the 3D correlation functions of interaction sites of solvent molecules around a solute of arbitrary shape. In the present article, we propose a SCF combination of the *ab initio* molecular orbital (MO) methods and 3D-RISM approach. A benchmark result for carbon monoxide in ambient water is also presented.

I-R-5 Which Carbon Oxide is More Soluble? *Ab initio* Study on Carbon Monoxide and Dioxide in Aqueous Solution

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[*Chem. Phys. Lett.* **323**, 257 (2000)]

In disagreement with an intuitive prediction on the basis of the molecular size and dipole moment, it is observed empirically that the solubility of carbon dioxide (CO₂) in water is larger than that of carbon monoxide (CO). In order to shed light on this puzzling behavior, the solvation free energy of CO and CO₂ in aqueous solution is studied by means of the RISM-SCF/MCSCF method, a combined *ab initio* molecular orbital theory and statistical mechanics theory of molecular liquids. It is shown that the specific hydrogen bonding between oxygen atoms in CO₂ and water molecules makes CO₂ more soluble.

I-R-6 NMR Chemical Shifts in Solution: A RISM-SCF Approach

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[*Chem. Phys. Lett.* **325**, 668 (2000)]

The NMR chemical shift induced by solvation is formulated based on the ab initio electronic structure theory coupled with the integral equation method of molecular liquids. In order to examine the validity of the theory, the chemical shift of the atoms in a water molecule in water is calculated. The preliminary result with respect to hydrogen gives a reasonable account for the solvation shift, and for its temperature and density dependence.

I-R-7 Electron Self-Trapping in Two Dimensional Fluid

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[*Chem. Phys. Lett.* **326**, 199 (2000)]

The behavior of an excess electron in two 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 of a 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 three causes: The excluded volume effect due to solvent, the pair attractive interaction between the electron and a solvent atom, and a balance of the attractive interactions from different solvent atoms.

I-S 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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I-S-1 Salt Effect on Stability and Solvation Structure of Peptide: An Integral Equation Study

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[*Bull. Chem. Soc. Jpn.* **73**, 1113 (2000)]

Salt effects on the stability and on the solvation structure of a peptide in a variety of aqueous solutions of the alkali-halide ions are studied by means of the reference interaction site model (RISM) theory. The order of salt effect on the peptide stability is consistent with the experimental results; the order follows the Hofmeister series. The results are further analyzed in order to clarify the nature of the salt effect which determines the Hofmeister series and to find the reason

why the Hofmeister series applies so generally to a variety of solutes in aqueous solutions. A heuristic model for explaining salt effects on the solvation structure of the peptide is proposed based on changes in the peptide-water pair correlation functions due to the ion perturbation.

I-S-2 Theoretical Study for Partial Molar Volume of Amino Acids in Aqueous Solution: Implication of Ideal Fluctuation Volume

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[*J. Chem. Phys.* **112**, 9469 (2000)]

A Kirkwood-Buff equation for the partial molar volumes of polyatomic molecules in solutions are

derived based on the reference interaction site model (RISM) theory of molecular liquids. The partial molar volume of the twenty amino acids in aqueous solution at infinite dilution are calculated using the equation, and the results are discussed in comparison with the experimental data. The results indicate that ionizations of the C- and N-terminus groups give negative contributions to the volume ranging from $-3.2 \text{ cm}^3/\text{mol}$ to $-9.7 \text{ cm}^3/\text{mol}$ depending on the amino acid. Ionization of the dissociable residues also give negative contribution which ranges from $-3.0 \text{ cm}^3/\text{mol}$ to $-6.0 \text{ cm}^3/\text{mol}$. On the other hand, contribution of the fractional charges on atoms to the volume is not necessarily negative, but rather slightly positive with

few exceptions. It is clarified that contribution from an atom group to the volume is largely dependent on the situation where the group is placed. Therefore, it is concluded that the conventional way of determining the partial molar volume from group contributions is not reliable. The theoretical results for the partial molar volume exhibit a systematic deviation from corresponding experimental data, which increases nearly proportionally with increasing temperature and with the number of atoms in the amino acids. In order to account for the deviation, a concept of the "ideal fluctuation volume" is proposed, which is the ideal gas contribution to the volume, originating from the intramolecular fluctuation of solute.

I-T 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-T-1 Relaxation of Average Energy and Rearrangement of Solvent Shells in Various Polar Solvents in Connection with Solvation Dynamics: Studied by RISM Theory

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

We employ a reference interaction-site model (RISM) theory to estimate the relaxation dynamics of average energy of solute-solvent systems as well as time-dependent radial distribution functions of solvents viewed from the solute. The theoretical results indicate that the rearrangement of the second solvent shell is about an order of magnitude slower compared with that of the first shell. We suggest that the slower relaxation of further solvent shells can play a significant role for

the dynamic relaxation of the inhomogeneous spectral width, which has been observed in our previous experiments of the time-resolved hole-burning and fluorescence spectroscopy.

I-T-2 Importance of Acoustic Solvent Mode and Solute-Solvent Radial Distribution Functions in Solvation Dynamics: Studied by RISM Theory

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

We have applied the reference interaction-site model (RISM) theory to explain our experiments on solvation dynamics of laser dyes in polar organic solvents by means of the transient hole-burning and time-resolved fluorescence spectroscopy [K. Nishiyama and T. Okada,

J. Phys. Chem. A **101**, 5729 (1997); **102**, 9729 (1998)]. The experiments show that the dynamic response function of the relaxation derived from the inhomogeneous spectral band-width of the solute–solvent system relaxes about an order of magnitude slower than that of average energy of the system. On the basis of our

present theoretical prediction, we suggest that the relaxation dynamics of the spectral width might be mainly characterized by the solvent acoustic mode (translational motion) as well as the rearrangement of second plus further solvent shells.

I-U 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.¹⁾ The surface enhanced infrared absorption spectroscopy has provided detailed picture regarding the orientation of water molecules at the surface.²⁾ 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.³⁾ 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-U-1 Potentials of Mean Force of Simple Ions in Ambient Aqueous Solution. I. Three-Dimensional Reference Interaction Site Model Approach

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[*J. Chem. Phys.* **112**, 10391 (2000)]

We adapt the three-dimensional reference interaction site model (3D-RISM) to calculate the potentials of mean force for ion–molecular solution as a difference between the chemical potential of solvation of a cluster of solutes and of individual ones. The method yields the solvation structure around the cluster of solutes in detail. The solvation chemical potential is obtained for the three-dimensional hypernetted chain (3D-HNC) closure as well as for its partial linearization (3D-PLHNC approximation). The solvation chemical potential is obtained in a closed analytical form for both the 3D-HNC and 3D-PLHNC closures. The 3D-RISM integral equations are solved by using the supercell technique. A straightforward supercell treatment of ionic solute in polar molecular solvent leads to a big

error in the potential of mean force as well as the solvation chemical potential, which for simple ions in water amounts to about 35 kcal/mol. We elaborated corrections to the 3D-RISM integral equations, alleviating the artifact of the supercell periodicity with an accuracy of 0.05 kcal/mol or better and restoring the long-range asymptotics of the solute–solvent correlation functions. The dielectrically consistent site–site RISM/HNC theory (DRISM/HNC) is employed for the solvent correlations to provide a proper description of the dielectric properties of solution. This allowed us to extend the description to solution at a finite salt concentration. We converge both the 3D-RISM and site–site DRISM integral equations by using the method of modified direct inversion in the iterative subspace.

Owing to the proper initial guess of the correlation functions, iteration begins at once for a given temperature and full molecular charge, avoiding a gradual decrease of the temperature and increase of the site charges, which greatly reduces the computation time. We calculate and discuss the potentials of mean force for sodium chloride in ambient water at infinite dilution as well as at a finite concentration.

I-U-2 Potentials of Mean Force of Simple Ions in Ambient Aqueous Solution. II. Solvation Structure from the Three-Dimensional Reference Interaction Site Model Approach, and Comparison with Simulations

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[*J. Chem. Phys.* **112**, 10403 (2000)]

We applied the three-dimensional reference interaction site model (3D-RISM) integral equation theory with the 3D hypernetted chain (3D-HNC) closure or its partial linearization (3D-PLHNC) to obtain the potentials of mean force (PMFs) and the solvation structure of sodium chloride in ambient water. The bulk solvent correlations are treated by the dielectrically consistent site-site RISM/HNC theory (DRISM/HNC) to provide a proper description of the dielectric properties of solution and to include the case of a finite salt concentration. The PMF is calculated as a difference in the solvation free energy of an ion pair and of individual ions. We obtained and analyzed in detail the PMFs and solvation structure for ion pairs of NaCl at infinite dilution and a concentration of 1 M. The results are in reasonably good agreement with molecular dynamics simulations for the same model of the solution species. Positions and orientations of water molecules in the first solvation shell around the ion pair are deduced. The short-range hydration structure of the ion pairs at infinite dilution and at moderate concentration is very similar. Ionic ordering and clustering is found in 1 M solution.

I-U-3 Hydration Free Energy of Hydrophobic Solutes Studied by a Reference Interaction Site Model with a Repulsive Bridge Correction and a Thermodynamic Perturbation Method

KOVALENKO, Andriy; HIRATA, Fumio

[*J. Chem. Phys.* **113**, 2793 (2000)]

We modify the site-site as well as three-dimensional (3D) versions of the reference interaction site model (RISM) integral equations with the hypernetted chain (HNC) closures by adding a repulsive bridge correction (RBC). The RBC treats the overestimation of water ordering around a hydrophobic solute in the RISM/HNC approximation, and thus refines the entropic component in the hydration free energy. We build up the bridge functions on r^{-12} repulsive core potentials, and propose RBC expressions for both the site-site and 3D-RISM approaches. To provide fast calculation, we obtain the excess chemical potential of hydration by using the thermodynamic perturbation theory (TPT). The site-site RISM/HNC+RBC as well as 3D-RISM/HNC+RBC approaches are applied to calculate the structure and thermodynamics of hydration of rare gases and alkanes in ambient water. For both approaches, the RBC drastically improves the agreement of the hydration chemical potential with simulation data and provides its correct dependence on the solute size. For solutes of a nonspherical form, the 3D treatment yields the

hydration structure in detail and better fits simulation results, whereas the site-site approach is essentially faster. The TPT approximation gives the hydration thermodynamics in good qualitative agreement with the exact results of the thermodynamic integration, and substantially reduces computational burden. The RBC-TPT approximation can improve the predictive capability of the hybrid algorithm of a generalized-ensemble Monte Carlo simulation combined with the site-site RISM theory, used to describe protein folding with due account for the water effect at the microscopic level. The RBC can be optimized for better fit to reference simulation data, and can be generalized for solute molecules with charged groups.

I-U-4 Liquid Structure at Metal Oxide-Water Interface: Accuracy of a Three-Dimensional RISM Methodology

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[*Chem. Phys. Lett.* **320**, 186 (2000)]

We calculated the structure of water in contact with the MgO 100 surface by using the three-dimensional reference interaction site model 3D-RISM integral equation theory. The spatial distributions of water oxygen and hydrogen over the surface unit cell are calculated and discussed. The water density profiles and the orientations obtained are in good agreement with computer simulations for the same model of the interface. The 3D-RISM approach shows considerable promise as a constituent of a self-consistent description of chemical processes at a metal oxide-water interface.

I-U-5 Self-Consistent, Kohn-Sham DFT and Three-Dimensional RISM Description of a Metal-Molecular Liquid Interface

KOVALENKO, Andriy; HIRATA, Fumio

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

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.