

RESEARCH ACTIVITIES VII

Department of Computational Molecular Science

VII-A Computer Simulation

VII-A-1 Path Integral Influence Functional Theory of Dynamics of Coherence between Vibrational States of Solute in Condensed Phase

MIKAMI, Taiji; OKAZAKI, Susumu

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Path integral influence functional theory has been applied to the dynamics of coherence between vibrational states of solute in condensed phase. First, time evolution of the off-diagonal term of the reduced density matrix $\rho_{mm}(t)$ was algebraically described by the cumulant expansion of the perturbative influence functional. Then, the theory is compared with the Redfield theory, rearranging the present description in a familiar way to that found in the Redfield theory. A numerical example of the theory is presented for the vibrational dynamics of cyanide ion in water assuming a coherent state $(|1+\sqrt{2}\rangle(|0\rangle+|1\rangle))$ at $t=0$. We find that $\text{Re}\rho_{10}(t)$ oscillates with high frequency and shows a fast damping. Relaxation time of the oscillation amplitude is estimated to be 5.1 ps for a certain configuration of the solution. Then, secular approximation often used in the Redfield theory is found to work well, at least, in the present system. Population relaxation time for the first excited state and pure dephasing time may also be calculated from the component of $\text{Re}\rho_{10}(t)$ to be 7.9 ps and 7.5 ps, respectively. Further, many-particle measurement for $\text{Re}\rho_{10}(t)$ gives the relaxation rate about three times faster than the single-measurement above. This comes from the inhomogeneity of the solute environment. We also calculated $\text{Re}\rho_{11}(t)$ and found the fast oscillation in the diagonal part of the density matrix $\text{Re}\rho_{11}(t)$. This oscillation is generated only when the initial density matrix includes the coherence.

VII-A-2 Mixed Quantum-Classical Molecular Dynamics Study of Vibrational Relaxation of CN^- Ion in Water: An Analysis of Coupling as a Function of Time

SATO, Masahiro; OKAZAKI, Susumu

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

Mixed quantum-classical molecular dynamics method has been applied to vibrational relaxation of CN^- in water, where coulombic force is predominant in the interaction. The calculation demonstrated that time-dependent interaction between the solute vibrational degree of freedom and the solvent water shows random-noise-like behavior, no collisional or stationary coupling observed in gas or solid, respectively, being found. This is in contrast to short-ranged-force system where the collision plays a dominant role in the relaxation. The interaction has been analyzed in detail as a function of time defining the effective coupling for the relaxation.

VII-A-3 Vibrational Relaxation Time of CN^- Ion in Water Studied by Mixed Quantum-Classical Molecular Dynamics: Comparison with Fermi's Golden Rule and Influence Functional Theory

SATO, Masahiro; OKAZAKI, Susumu

[*Mol. Sim.* in press]

Mixed quantum-classical molecular dynamics method has been applied to vibrational relaxation of CN^- in water. The calculated relaxation time was compared with those based upon Fermi's golden rule with classical interaction and influence functional theory with classical bath. They are in good agreement with each other. Flexible water model adopted here enhanced the relaxation rate by a factor of about 5 compared with the rigid rotor model. This supports our previous result of path integral influence functional theory that intramolecular bending of water plays an essential role in the relaxation.

VII-B Molecular Dynamics Study of Classical Complex Systems

VII-B-1 Molecular Dynamics Studies of Self-Organization of Amphiphilic Molecules in the Aqueous Solution

YOSHII, Noriyuki; IWAHASHI, Kensuke;

YAMADA, Atsushi; OKAZAKI, Susumu

Self-organization of amphiphilic molecules in water such as micelles and lipid bilayers is investigated. Potential of mean force between amphiphilic molecules

is a target of this investigation. In order to accomplish this, general purpose program for large-scale molecular dynamics calculation has been coded in a suitable way for very highly parallel computing and grid computing. The program can be used to execute a calculation for the

system of a million of atoms with arbitrary molecular configurations. Preliminary calculations have been done for many-body effect on the potential of mean force among small hydrophobic solutes.

VII-C Development of Simulation Algorithms for Quantum Many-Body Systems

VII-C-1 On the Solvation Structure of a Rare-Gas Solute in Superfluid Helium-4

MIURA, Shinichi

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

Path integral hybrid Monte Carlo calculations have been performed for a system consisting of a single neon atom in the superfluid helium. An expression of the local superfluid density around the solute atom is introduced to analyze the microscopic density fluctuation around the solute in detail. We show that the superfluid component in the solvation shell dramatically increases with lowering temperature, although the radial number density profile itself is almost independent of temperature. We also compare the local superfluid density calculated by our expression with that by another commonly used one. Although both local superfluid densities show similar trend as a function of the radial distance from the solute atom, quantitative differences are found; the superfluid component is underestimated by the commonly used one. This is due to the fact that the commonly used definition of the local superfluid density does not give the bulk superfluid density by integrating it over whole space. New expression introduced in the present study is free from such a deficiency.