Computer Center

VIII-W Computer Simulation of Quantum Systems in Condensed Phase

VIII-W-1 Vibrational Energy Transfer from Solute to Solvent: An Analysis Based upon Path Integral Influence Functional Theory and Mixed Quantum-Classical Molecular Dynamics Method

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Path integral influence functional theory and mixed quantum–classical molecular dynamics method have been applied to the analysis of molecular mechanism of solute vibrational energy relaxation in solution. A numerical example is CN^- ion in water.

First, quantum effect of the solvent has been examined by taking a zero limit of Planck constant relevant to the solvent degrees of freedom. The effect is unexpectedly great. Classical approximation for the solvent significantly overestimates the relaxation time. The degree of the overestimation depends much upon the process, *e.g.* single-phonon, two-phonon, and three-phonon processes. However, it is interesting to find that it affects little energy dissipation path. Second, in order to obtain a microscopic picture of the relaxation in terms of molecular motion, couplings between normal mode and the solute were divided into contributions from each water molecule. Couplings spread over the normal modes are not localized within particular modes. However, in molecular language, molecules in the first hydration shell are mostly responsible for the energy flow from the solute. Third, the couplings actually found in the solution have also been analyzed as a function of time. The solvent does not show delta-function-like coupling. This indicates that the system does not relax by collision which is usually found in the gas state. The coupling in the solution oscillates very rapidly. Then, matching of both transition frequency and phase between the interaction and the wave function of the system were found to be important. In a short time scale, we cannot find any systematic behavior of the coupling. It looks like random. However, integrating the coupling over pico second, the system shows relaxation to the ground state to a certain extent. The relaxation rate changes in hundred femto second or pico second reflecting the structural change of the hydration shell.

VIII-X Molecular Dynamics Study of Classical Complex Systems

VIII-X-1 A Molecular Dynamics Study of Water Penetration into Biomembrane

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Free energy profile of water penetration into lipid bilayer has been evaluated based upon molecular dynamics calculations combined with thermodynamic integration method. The calculated profile for 25 arbitrarily chosen penetration paths shows that the free energy barrier height has a wide distribution, demonstrating a sort of selectivity of the path by water molecule. Structure of the path or structure of the surrounding lipid molecules was examined in order to extract a factor which determines the barrier height.

VIII-X-2 Molecular Dynamics Study of Mechanical Extension of Polyalanine by AFM Cantilever

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A series of molecular dynamics calculations have been performed mimicking the mechanical extension of α-helical polyalanine molecule in water on the AFM. Force profile has been evaluated as a function of extension. In an initial stage of the extension, ~ 5%, the force was found to follow the Hooke’s law up to about 140 pN. At the extension of about 10%, however, the restoring force diminishes, indicating the rupture of α-helix. Then, α-helix region and β-strand region separate from each other in one molecule. Further extension causes stepwise breakages of hydrogen bonds to give the wholly β-stranded polyalanine.