Free Energy of Solvation in the Method of Energy Representation

N. Matubayasi[C,S]
Kyoto University, Kyoto, Japan
nobuyuki@scl.kyoto-u.ac.jp

The most fundamental quantity used to describe a process in a solution is the free-energy change. The free-energy change which includes the solvent effect is the solvation free energy. In the present work, we develop a functional for the solvation free energy of a solute in solution and apply it to frontline topics of physical chemistry. We introduce the energy representation, and provide an approximate but accurate functional which is expressed in terms of energy distribution functions in the solution and pure solvent systems of interest. In the energy representation, the solute-solvent distribution is expressed over the one-dimensional coordinate specifying the solute-solvent interaction energy. The functional for the solvation free energy is then constructed by adopting the Percus-Yevick-like and hypernetted-chain-like approximations in the repulsive and attractive regions of the solute-solvent interaction, respectively. The functional is exact to the second order in density and is suitable to treat supercritical fluids. It is demonstrated that the solvation free energies of nonpolar, polar, and ionic solutes in water are evaluated accurately and efficiently from a single functional in both ambient and supercritical conditions. Furthermore, the system homogeneity, thermodynamic limit, the molecular rigidity is not assumed in the formulation, and the method is found to work well for molecules with intramolecular flexibility and for inhomogeneous and/or finite systems. The applications to hydrothermal chemical reactions and solubilization due to micelle formation will be presented.