COSMO-RS: The Bridge from Quantum Chemistry to Fluid Phase Thermodynamics

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Due to the rapid developments of methods and computers, reliable quantum chemical calculations on molecules of up to 50 - 100 atoms can nowadays be performed within the time-scale of a day on cheap computer hardware. Thus quantum chemistry, and here especially the density functional theory (DFT), has become an efficient source of information for molecular properties. Nevertheless, the traditional quantum chemistry is restricted to the calculation of single molecules in vacuum or to small clusters. Hence it cannot be directly used for the calculation of properties of molecules in liquids or even for fluid phase equilibrium properties.

In this situation, dielectric continuum solvation methods such as PCM or COSMO have become quite popular. In this talk I will specially focus on the extension of COSMO by a combination with statistical thermodynamics, COSMO-RS. This provides an efficient link between quantum chemistry and fluid phase thermodynamics. COSMO-RS starts from a quantum chemical DFT/COSMO calculation for each chemical species under consideration, i.e. for solutes and solvent molecules, in which each molecule is treated as if embedded in a perfect conductor. This state of ideal electrostatic screening is used as reference point for the consideration of molecules in the liquid phase. All energies are expressed relative to this state, and interaction energies of molecules in solution are described as contact interactions of ideally screened molecular surface pieces. All interactions are quantified by the screening charge densities on the adjacent surface pieces. Combined with an extremely efficient and nevertheless exact statistical thermodynamics algorithm of pair-wise interacting surfaces, this description of molecular interactions in solution enables the calculation of the chemical potentials, i.e. the activity coefficients, of almost arbitrary solutes in almost arbitrary solvents, even in multi-component mixtures. Finally this enables the calculation of phase diagrams of liquid systems, i.e. of activity coefficients, vapor pressures, excess free energies and enthalpies. COSMO-RS can be applied not only to neutral systems, but as well to charged species, i.e. to electrolyte systems, pKa-calculation, and even to complex systems as ionic liquids, micelles, bio-membranes and recently to drug-enzyme interactions.

COSMO-RS has been established as a third, independent access to predictive molecular thermodynamics in between the conventional group contribution methods and the force-field based molecular dynamics and Monte-Carlo simulations, and opens a lot of novel opportunities for applications which are hardly doable by the other methods. In addition, the vividness of the COSMO-RS surface interaction description makes it very suitable for teaching molecular thermodynamics.