

Molecular Density Functional Theory of Water

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The determination of the solvation free energy and the microscopic structure of complex solutes in molecular solvent is an important problem for the understanding of chemical and biological systems. This can be done by the use of molecular simulation techniques such as Monte Carlo and Molecular Dynamics with explicit molecular solvent molecules to sample the microscopic solvent configurations. The use of thermodynamic integration techniques such as umbrella sampling enables to evaluate the free energy of the system. Another route is to employ implicit solvent methods, which do not consider explicitly all the instantaneous microscopic configurations of solvent molecules but instead treat it in a continuous way, while still taking into account its molecular nature. The computational cost of the implicit methods is then much lower than the one of molecular simulations. Molecular density functional theory [1] (MDFT), an implicit solvent method that can predict both microscopic structure and thermodynamic properties of any solute in a molecular fluid is introduced. Molecular DFT has many features in common with electronic density functional theory; they will be highlighted in this presentation. This theory relies on the fact that the grand potential of a molecular fluid submitted to an external potential could be written as a functional of the position and orientation solvent density. The exact free energy functional is obviously not known but approximations can be proposed. Due to the tetrahedral order of the fluid, the study of water raises particular problems that require some extra corrections [2]. A functional appropriate to liquid water [3] will be proposed and some results on the hydration properties of a set of solutes (atomic, molecular, charged and non charged) in water will be presented to prove the validity of the approximations made.

REFERENCES

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