

Using Molecular Density Functional Theory to study electron transfer reaction in water

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The Marcus theory of charge transfer reactions in solution has provided a very simple two-chemical state picture, based on two intersecting parabola [1]. It has been widely used in the electrochemical community because it made possible to understand the experimental data, to interpret them quantitatively but also to make predictions. Originally, the theory modeled the solvent by a dielectric continuum. The response of the solvent to the charged solute is linear which implies that the free energy curves of the reactant and product are quadratic, with the same curvature. The validity of this assumption can be tested by computer simulations, either using force field molecular dynamics (MD) or *ab-initio* MD [2]. However, this is rather costly since it requires to continuously transform the reactants into products to have a proper sampling of the solvent configurations, thus it is necessary to run several simulations to study one electron transfer reaction. Most of the computational times being spent to compute solvent-solvent interaction, it seems promising to have an implicit description of the solvent.

I will introduce Molecular Density Functional Theory (MDFT), an implicit solvent method that retains the molecular description of the solvent [3]. In this framework, a functional of the spatial and orientational solvent density is defined. This functional can be minimized with respect to the solvent density and it equals the solvation free energy at its minimum which is reached for the equilibrium solvent density. This procedure allows to access the solvation free energy in water of any given solute with a computational cost that is several orders of magnitude lower than MD.

Following the framework that has been proposed for Reference Interaction Site Model (RISM) [4], another implicit solvent method, I will show how MDFT can be used to study simple electron transfer reaction and address the validity of Marcus theory assumptions. The drastic reduction in computational cost would allow to efficiently and systematically tackle systems for which MD simulations would be challenging [5].

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