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Alignment of electronic energy levels at electrochemical interfaces

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The thermodynamic energy levels (adiabatic ionization potentials) of electroactive species and electrode determine the reversible potential of an electrode reaction. A full electrochemical energy level diagram should however also compare the corresponding vertical energy levels. Information on vertical ionization potentials and electron affinities is needed because vertical energy gaps control the activation barriers, and hence the overpotential. The difference between the adiabatic and vertical energy levels is due to solvent reorganization, which can be an important effect in particular for electron transfer reactions taking place in the outer Helmholtz plane or for species adsorbed on metal oxide electrodes.

Computational schemes for the construction of electrochemical energy level diagrams should therefore be very general, capable of treating the adiabatic as well as vertical energy levels of both homogenous and heterogeneous redox reactions. We have developed such a scheme combining density functional theory based molecular dynamics (DFTMD) and free energy perturbation (FEP) methods[1]. The key feature of this method is that solute species, solvent and solid electrode are treated at the same level of theory ("all-atom" approach). Ionization energies are directly referred to the standard hydrogen electrode (SHE) using the work function of the proton as energy reference. The work function of the proton is computed from the free energy for reversible insertion of a proton in the DFTMD model. This procedure, while computationally rather costly, has the advantage that it can be equally used to compute acidity constants (pKa) which is crucial for the study of proton coupled redox reactions[2].

In this talk we will review the application of the DFTMD/FEP method to the energy level diagrams of two popular electrochemical interfaces, the Pt(111)-water interface[1] and rutile TiO_2(110)-water interface[1,2]. The first is a model system for the study of electrocatalysis, the second for photocatalysis. Coupled together they form a cell for photoelectrochemical water splitting. These materials span a wide range of electronic properties from a metal (Pt), a wide gap semiconductor(TiO_2) to an insulating oxide (water). The differences in electronic structure are reflected in an increasing tendency to localize ("solvate") excess or missing electrons (holes). This is a central theme of the talk. Related to this, unfortunately, is the deteriorating performance of the DFT approximation, with water as the worst case[3]. This is of obvious concern for the application of an all-atom approach because water is a common component in electrochemical cells. The talk ends with brief outlook how these difficulties can be overcome.

References

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