FPMD construction of pH-Eh diagram

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Acidity constant (pKa) and redox potential (U^0) are the fundametal thermodynamic quantities to construct pH-Eh diagrams. The traditional static quantum chemistry method ignores the details of the solvent and therefore hard to be applied at the P-T conditions of geofluids. First principles molecular dynamics (FPMD), treating both the solvent and the solute at the same quantum mechanical level, provides a feasible way to estimate pKa and U0 at elevated P-T conditions.

This contribution will introduce our recent progress in the calculations of pKa and U^0 by using the FPMD based vertical energy gap method that combines FPMD with free energy perturbation technique. Extensive tests indicate that both generalized gradient approximation (GGA) and hybrid functionals reproduce the pKas with an acceptable accuracy. In contrast, the U^0 by GGA can be too low by over 1 V. It is found that GGA can exaggerate the mixing of the electronic states of the solute with the valence band of liquid water, causing underestimation of U0 of the solute. Hybrid functionals improves the prediction of the band states of liquid water, that eventually leads to considerable improvement of the redox potentials. After a short introduction of the techniques, we will show the pKas results of small molecular acids and metal aqua-cations and the U0s of organic radicals and transition metal aqua-cations.