Surface Studies with Combined Free Energy Functionals of Electronic and Liquid Densities

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The microscopic structure of both a solid surface and a contacting liquid can be dramatically affected by the interaction between the two systems, particularly at the interface between a polar surface and a polar liquid. We present a study of oxide and metallic surfaces in a liquid environment with Joint Density Functional Theory (JDFT) [1], a computationally efficient alternative to molecular dynamics simulations which replaces thermal sampling with a single variational principle for the free energy of the full system. Within the rigorous framework of JDFT, we introduce classical density-functionals for ionic species and describe how to couple them with existing functionals for liquid water and traditional electronic density-functionals. Calculations were performed within the open source software package JDFTx [2] and employ a liquid water functional, which captures bulk properties and microscopic structure over the entire phase diagram of the liquid [3], and a density-only coupling functional between the electronic and liquid systems [4]. With this microscopically accurate description of the liquid-solid interface structure, we study the voltage-dependent behavior of transition metal electrodes in an aqueous electrolyte environment and show qualitative agreement with experiment [5]. We additionally predict the structure of water at a rutile TiO_2 (001) surface and investigate the effects of solvation on the electronic properties of the system. In each case, we gain physical insight which could direct future studies of catalysis and electrode stability in electrochemical systems.

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