Joint Density Functional Theory: An Approach to Ab-Initio Continuum Solvation

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We review the background of Joint Density Functional Theory (JDFT),[1,2,3] an in principle exact ab-initio continuum solvation theory based on the concepts of DFT. We will present advances in approximate functionals particularly for the liquid, as functionals for liquid water are surprisingly poorly developed despite its importance. Our theory allows simulation of a variety of materials, such as intermetallics and complex oxides, in contact with a fluid environment.

We also present results for a computationally efficient approximate functional capturing the key electrostatic interactions between electronic systems and an ionic liquid environment. We demonstrate how DFT calculations can address the fundamental physical issues underlying electrochemistry, including the definition of a consistent reference potential, the treatment of charged surfaces under periodic boundary conditions, and the study of the electrode-electrolyte interface as a function of the applied potential. Results for interfacial capacitances and potentials of zero charge calculated using these techniques will be compared to experimental values.

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[3] J. Lischner and T. A. Arias, J. Phys. Chem. B **114**, 1946-1953 (2010).