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Ab initio joint density-functional theory of solvated electrodes, with model and explicit solvation[1]

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First-principles guided design of improved electrochemical systems has the potential for great societal impact by making non-fossil-fuel systems economically viable. Potential applications include improvements in fuel-cells, solar-fuel systems ("artificial photosynthesis"), supercapacitors and batteries. Economical fuel-cell systems would enable zero-carbon footprint transportation, solar-fuel systems would directly convert sunlight and water into hydrogen fuel for such fuel-cell vehicles, supercapacitors would enable nearly full recovery of energy lost during vehicle braking thus extending electric vehicle range and acceptance, and economical high-capacity batteries would be central to mitigating the indeterminacy of renewable resources such as wind and solar. Central to the operation of all of the above electrochemical systems is the *electrode-electrolyte interface*, whose underlying physics is quite rich, yet remains remarkably poorly understood. The essential underlying technical challenge to the first principles studies which could explore this physics is the need to properly represent *simultaneously both* the interaction between electron-transfer events at the electrode, which demand a quantum mechanical description, *and* multiscale phenomena in the liquid environment such as the electrochemical double layer (ECDL) and its associated shielding, which demand a statistical description. A direct *ab initio* approach to this challenge would, in principle, require statistical sampling and thousands of repetitions of already computationally demanding quantum mechanical calculations. This talk will begin with a brief review of a recent advance, joint density-functional theory (JDFT), which allows for a fully rigorous and, in principle, exact representation of the thermodynamic equilibrium between a system described at the quantum-mechanical level and a liquid environment, *but without the need for costly sampling*[2,3]. We then shall demonstrate how this approach applies in the electrochemical context and how it is needed for realistic description of solvated electrode systems[4], and how simple "implicit" polarized continuum methods fail radically in this context. Finally, we shall present a series of results relevant to battery, supercapacitor, and solar-fuel systems, one of which has led to a recent invention disclosure for improving battery cycle lifetimes.

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