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A Priori **Method for First Principles Study of Aqueous Electrochemistry: Application to Biofuels and Catalysis** KENDRA LETCHWORTH WEAVER, RAVISHANKAR SUNDARARAMAN, TOMAS ARIAS, Cornell University — We present a novel description of water which will allow the first *a priori* studies of catalysis of biofuels in aqueous electrochemical environments. Our method offers a computationally efficient alternative to the thermal sampling required by molecular dynamics yet provides a more realistic description of bulk water than including explicit frozen water or traditional continuum solvation models. Into Joint Density Functional Theory (JDFT), which joins an electron density-functional for the solute with classical density-functional theories for liquid water[1] into a single variational principle for the free energy of the combined system, we introduce the innovation of an *a priori* form of the coupling functional between the quantum-mechanical system and liquid water based on a local density approximation to the Hohenberg-Kohn density-only functional. Without any fits to solvation data whatsoever, this new method predicts solvation energies of small organic molecules well compared to state-of-the art empirical quantum-chemical cavity approaches. The site interaction potentials produced closely resemble the widely used TIP3P site potentials for water without requiring any empirical parameters.

[1]R. Sundararaman et al, unpublished, to be presented at the APS March Meeting (2011)

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