

Abstract Submitted
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Understanding the spurious DFT fractional charge in the electrochemical double layer LEANNE CHEN, MICHAL BAJDICH, ALAN LUNTZ, KAREN CHAN, JENS NORSKOV, SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator Laboratory and Stanford University — An ongoing challenge in computational electrochemistry is the accurate determination of electrochemical barriers at constant electrode potential. Recently, our group developed an efficient scheme to determine the barriers using a simple extrapolation based on the interfacial charge [1]. However, semilocal DFT calculations have shown that the magnitude of the charge of solvated species (H_3O^+ , OH^- , Li^+ , Na^+) in the outer Helmholtz plane is not $1e$, but always near $0.6e$, which suggests a charge delocalization error in DFT. Furthermore, we frequently observe inaccurate alignment of the metal Fermi and solvent energy levels. Using an increasing amount of exact exchange, we first analyze the charge delocalization error in the dissociation of NaCl molecule, where a large amount of exchange is needed to reproduce the step-like transition of charge from $+1$ to 0 on the dissociated Na and Cl. Next, we apply the same method to the metal-water interface with solvated ions at varying distances from the surface. The performance of hybrid and other fractional charge-corrected functionals will be discussed together with the possibility of a simple correction scheme. [1] Chan, K.; Nørskov, J. K. Electrochemical Barriers Made Simple. *J. Phys. Chem. Lett.* **2015**, *6* (14), 2663–2668.

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