

Abstract Submitted
for the MAR12 Meeting of
The American Physical Society

Electronic density functional theory in the grand canonical ensemble, electrochemistry, and the underpotential deposition of Cu/Pt(111)¹ RAVISHANKAR SUNDARARAMAN, KENDRA WEAVER, TOMAS ARIAS, Physics Department, Cornell University — The study of electrochemical systems within electronic density functional theory requires the handling of non-neutral electronic systems in the plane-wave basis in order to accurately describe charged metallic surfaces; this can be accomplished in joint density functional theory by adding an electrolyte with Debye screening ². This capability opens up the opportunity to work in the grand canonical ensemble at fixed chemical potential μ for the electrons, which corresponds directly to the experimental setting in electrochemistry. We present efficient techniques for electronic density functional calculations at fixed μ , and demonstrate the improvement in predictive power over conventional neutral calculations using the underpotential deposition of Cu/Pt(111) as an example: for the first time, we calculate absolute voltages for electrochemical processes in excellent agreement with experiment, instead of voltage shifts alone.

¹This work was supported as a part of the Energy Materials Center at Cornell (EMC2), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001086.

²K. L. Weaver and T. A. Arias (under preparation)

Ravishankar Sundararaman
Cornell University

Date submitted: 10 Nov 2011

Electronic form version 1.4