Electron-transfer diabatic free-energy surfaces from first-principles molecular dynamics

P. H.-L. Sit,1 Matteo Cococcioni,2 and Nicola Marzari2

1Department of Physics, Massachusetts Institute of Technology
Cambridge, MA 02139

2Department of Materials Science and Engineering, Massachusetts Institute of Technology
Cambridge, MA 02139

Electron-transfer processes are one of the most fundamental and intriguing chemical processes, whose importance ranges from electrochemistry to biochemistry to molecular electronics. We introduce here a general approach to calculate from first-principles the diabatic free-energy surfaces for electron-transfer reactions, based on Marcus theory1,2 and using first-principles molecular dynamics to include an accurate description of the energetics and thermodynamics of the active centers and the surrounding medium. Using the Marcus energy gap as a reaction coordinate, we construct the diabatic free-energy surfaces from umbrella sampling on large ensembles of configurations. The self-interaction problem in density-functional theory is addressed via a novel class of penalty functionals appropriate to the electron-transfer problem; these same functionals are used to assess the energy cost for an electron-transfer step against the driving force of the nuclear coordinates. As a paradigmatic case study, the self-exchange reaction between ferrous and ferric ions in solution is studied in detail.
