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Realistic, quantitative descriptions of electron-transfer reactions: diabatic free-energy surfaces from first-principles molecular dynamics P. H.-L. SIT, Department of Physics, Massachusetts Institute of Technology, M. COCOCCIONI, Department of Materials Science and Engineering, Massachusetts Institute of Technology, NICOLA MARZARI, Department of Materials Science and Engineering, Massachusetts Institute of Technology — A general approach to calculate the diabatic surfaces for electron-transfer reactions is presented, based on first-principles molecular dynamics of the active centers and their surrounding medium. The excitation energy corresponding to the transfer of an electron at any given ionic configuration (the Marcus energy gap) is accurately assessed within ground-state density-functional theory via a novel penalty functional for oxidation-reduction reactions that appropriately acts on the electronic degrees of freedom alone. The self-interaction error intrinsic to most exchange-correlation functionals is also corrected using the same penalty functional. The free-energy diabatic surfaces are then constructed with umbrella sampling on large ensembles of configurations. As a paradigmatic case study, the self-exchange reaction between ferrous and ferric ions in water is studied in detail.

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