Electron-transfer diabatic free energy surfaces from first-principles molecular dynamics P. H.-L. SIT, Department of Physics, MIT, Cambridge, MA 02139, MATTEO COCOCCIONI, DMSE, MIT, Cambridge, MA 02139, NICOLA MARZARI, DMSE, MIT, Cambridge, MA 02139 — Electron transfer in aqueous solution is a fundamental process in physical chemistry, and since the introduction of Marcus theory it has been extensively studied using classical force-fields molecular dynamics. However, classical potentials contain fitted parameters, and have obvious limitations in describing structural effects related to hybridization and electronic polarization. In this work, we investigate electron transfer fully from first-principles, using the case of ferrous-ferric ions solvated in water as a paradigmatic example. The structure and dynamics of the aqua ions at ambient conditions are studied via Car-Parrinello molecular dynamics. The diabatic free energy surfaces in the limit of two ions infinitely apart are calculated with umbrella sampling, obtaining parabolic free energy curves, in agreement with Marcus theory. The extension of our approach to ions at finite distances is also discussed, and our solution to the specific challenges that this problem entails, ranging from self-interaction effects to localization constraints.

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