

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

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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 theory^{1,2} 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.

- [1] R. A. Marcus and N. Sutin, *Biochim. Biophys. Acta* **881** 265 (1985).
- [2] For a review, see D. Chandler, in *Classical and Quantum Dynamics in Condensed Phase Simulation*, edited by B. J. Berne, G. Ciccotti and D. F. Coker (World Scientific, Singapore, 1998).