Title: The Simplest Possible Approach for Simulating $S_0$-$S_1$ Conical Intersections with DFT/TDDFT — Adding One Doubly Excited Configuration

Authors: Hung-Hsuan Teh and Joseph Subotnik

Abstract:
A simple combination of DFT/TDDFT and configuration interaction is presented to fix up the incorrect topology of the $S_0$-$S_1$ conical intersection (CI) and allow a description of bond making and bond breaking in photoinduced dynamics. The proposed TDDFT-1D method includes one lone optimized doubly excited configuration in addition to the DFT/TDDFT singly-excited states within the context of a large configuration interaction Hamiltonian. Results for ethylene and stilbene are provided to demonstrate that this ansatz can yield physically meaningful potential energy surfaces near $S_0$-$S_1$ avoided crossings, without changing the vertical excitation energies far from the relevant crossings. We also investigate the famous linear water example (Levine et al., Mol. Phys., 104, 1039 (2006)) to show that the algorithm calculates the correct topology of the $S_0$-$S_1$ CI and yields the correct geometric phase.