

Nonadiabatic dynamics in the condensed phase

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Most nonadiabatic processes in nature occur in condensed phase environments, yet their in silico modelling remains challenging. Explicit solvation substantially increases the system size, the number of excited states, and the number of nonradiative deactivation (NRD) pathways. Within the CP2K software package,[1] major efforts have been devoted to enabling explicitly solvation nonadiabatic molecular dynamics (NAMMD) with periodic boundary conditions (PBC). Our recent contributions include spin-flip time-dependent density functional theory (SF-TDDFT),[2] trajectory surface hopping algorithms (TSH), and delta self-consistent field (Δ SCF).[3-6] The latter approach is specifically aimed at improving the computational feasibility of NAMMD by reducing its cost to a level comparable to ground state DFT.

To illustrate the capabilities of the CP2K code, we performed TSH NAMMD simulations for three distinct photoexcited systems in aqueous solution. For cis- and trans-diimide, Δ SCF-based NAMMD shows that explicit solvation substantially increases the excited state lifetimes, particularly for the trans conformer as a result of stronger hydrogen bonding.[6,7] Solvent effects were examined similarly for cyclopropanone, where hydration equilibria increase system complexity.[8] While NRD pathways remain comparable between gas-phase and solvated systems, photolysis is reduced in solution.

TDDFT-based NAMMD simulations of ortho- and para-nitrophenol, including spin-orbit coupling, reveal a strong solvent-cage effect that constrains molecular flexibility, consequently inhibiting intersystem crossing (ISC). QM/MM treatment of the solvent yields NRD mechanisms more closely resembling those of the isolated system than those obtained with a fully quantum mechanical treatment of the solvent.

[1]CP2K, <https://www.cp2k.org/>

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