

Approximate vs. Exact Embedding for Excited-State Processes and Response Properties in Complex Systems

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The development of projection-based ("exact") subsystem TDDFT (sTDDFT) has enabled detailed analyses of the error sources in approximate sTDDFT versions. In previous work, we have used this framework to study, e.g., the influence of inter-subsystem charge-transfer excitations or subsystem-environment response couplings on spectroscopic properties. In particular, we could show that environment response couplings are essential for accurate predictions of chiroptical properties such as optical rotatory dispersion (ORD).

Here, we extend this analysis towards molecules in bulk solvent, modelled in terms of a sequential molecular dynamics and sTDDFT strategy. We focus on the convergence of ORD with respect to the solvation-shell size and to averaging of solvent conformations. In addition, we reconsider the role of short-range interactions in approximate sTDDFT calculations on coupled chromophores, based on comparisons with projection-based sTDDFT. We also outline how projection-based sTDDFT can be employed to study triplet excitation-energy transfer couplings in solution.

As a slight digression, we demonstrate how projection-based embedding can be exploited for the calculation of relative energies based on correlated wavefunction methods embedded in DFT environments. This also motivates related work on multi-level wavefunction methods.