

### Conical intersections in solution with polarizable embedding

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A popular approach to modelling complex systems is to use QM/MM; however, charge-transfer (CT) states demand a description of the electronic polarization of the environment, which is missed with simple electrostatic embedding. This can be captured with polarizable embedding (PE), wherein induced dipoles on the MM atoms respond to the charge distributions of the QM and MM regions. Of interest is PE's performance for conical intersections (CI), since these electronic-crossing funnels control the rate and product distributions of photochemical reactions. We showed previously that all popular types of PE exhibit artefacts at electronic crossings.

Building on an old idea from Thole, we developed an approach called integral-exact direct reaction field (IEDRF) that successfully describes CIs. The embedding potential contains zero, one, and two-electron contributions that correctly screen electron-electron repulsions and lead to the stabilization of CT states. Noting the 2e terms factorize as tensor products allows efficient plug-in compatibility with graphical processing unit implementations of many electronic structures, including CIS, TDDFT, CASCI, and CASSCF, as well as their analytical gradients.

We applied IEDRF to the purple bacteria reaction center (PBRC), in which the origin of unidirectional CT has long been under debate. IEDRF is seen to stabilize CT states by  $\sim 1$  eV compared to a non-polarizable QM/MM description, and correctly captures asymmetry between the inactive and active branches. Furthermore, we compute fields in quantitative agreement with vibrational Stark spectroscopy, supporting a picture of the unidirectionality that arises from different effective dielectric constants in the active vs inactive branches of PBRC.