Excited State Transition Energies and Properties in Solution from a Smooth Dielectric Model

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Abstract: A quantum mechanical solvation model is presented for a solute embedded in a polarizable dielectric medium, where the solute cavity is determined from an electronic isodensity surface in a smooth two-parameter model previously implemented in plane-wave-based density functional theory computations. In this work, solvent-solute interactions are incorporated into a Hartree-Fock framework and captured via numerical solution of the nonhomogenous Poisson equation on a real-space grid through an interface between PSI4 and the DL_MG multigrid solver library. The method is applied here to compute excited state transition energies and properties with the equation-of-motion coupled-cluster singles and doubles method (EOM-CCSD). Results are presented for solvated water, as well as formaldehyde, acetone and *trans*-acrolein, which have low-lying $n \rightarrow \pi^*$ transitions and associated blue shifts in aqueous solution. Comparisons are made with other theoretical approaches, including popular implicit solvation models and QM/MM methods, in addition to available experimental data.

CL05