

A Framework to Generalize Polarizable Continuum Models to Capture the Non-Local Dielectric Response of Solvents

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Polarizable continuum models [1–3], which replace the solvent by a dielectric cavity, are inexpensive approximations to solvent effects on the electronic structure of solvated systems. Despite the drastic approximation of replacing solvent molecules with a continuum at the atomic scale, these models reasonably capture ground-state solvation energies and to some degree, the solvent shifts in excited state spectra.

We present a generalization of the polarizable continuum model derived from a series of approximations within classical density functional theory for the rotational response, and from electronic density functional perturbation theory for the polarization response. This model naturally captures the non-local nature of the solvent dielectric response due to finite molecular size for rotations and the finite extent of the eigenfunctions of the susceptibility. We demonstrate applications of the resulting theory in density functional, coupled cluster and quantum Monte Carlo calculations. Additionally, we find significant improvements in the solvent shifts of excited states predicted by the GW method.

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