

Nonlocal polarizable continuum models from joint density-functional theory

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Ab initio calculations provide useful insights into the structure of matter and processes at the atomic scale. Delivering these benefits to the study of surface structures and reactions in solution is complicated by the need for thermodynamic phase-space sampling of the liquid environment. Continuum solvation models avoid the prohibitive cost of molecular dynamics methods and efficiently treat solvent effects, but typically at the price of empiricism.

Joint density functional theory (JDFT) provides a rigorous, in-principle exact framework for combining classical density functional theories of liquids with electronic density functional theory for a subsystem of interest. We briefly review practical approximations to JDFT that occupy the middle ground between molecular dynamics and traditional continuum solvation models, in rigor as well as in computational efficiency. We then derive a solvation model as a limit of JDFT, which includes nonlocal solvent response and matches the accuracy and efficiency of traditional polarizable continuum models without the empiricism. Finally, we demonstrate the capability of this theory to study chemistry in solution with a model electrochemical system.