Revised self-consistent continuum solvation in electronic-structure calculations

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The solvation model proposed by Fattebert and Gygi [J. Comput. Chem. 23, 662 (2002)] and Scherlis et al. [J. Chem. Phys. 124, 074103 (2006)] is reformulated, overcoming some of the numerical limitations encountered and extending its range of applicability. We first recast the problem in terms of induced polarization charges that act as a direct mapping of the self-consistent continuum dielectric; this allows to define a functional form for the dielectric that is well behaved both in the high-density region of the nuclear charges and in the low-density region where the electronic wavefunctions decay into the solvent. Second, we outline an iterative procedure to solve the Poisson equation for the quantum fragment embedded in the solvent that does not require multigrid algorithms, is trivially parallel, and can be applied to any Bravais crystallographic system. Last, we capture some of the non-electrostatic or cavitation terms via a combined use of the quantum volume and quantum surface [M. Cococcioni, F. Mauri, G. Ceder, and N. Marzari, Phys. Rev. Lett. 94, 145501 (2005)] of the solute. The resulting self-consistent continuum solvation model provides a very effective and compact fit of computational and experimental data, whereby the static dielectric constant of the solvent and one parameter allow to fit the electrostatic energy provided by the polarizable continuum model with a mean absolute error of 0.3 kcal/mol on a set of 240 neutral solutes. Two parameters allow to fit experimental solvation energies on the same set with a mean absolute error of 1.3 kcal/mol. A detailed analysis of these results, broken down along different classes of chemical compounds, shows that several classes of organic compounds display very high accuracy, with solvation energies in error of 0.3-0.4 kcal/mol, whereby larger discrepancies are mostly limited to self-dissociating species and strong hydrogen-bond-forming compounds. (C) 2012 American Institute of Physics.