Intermolecular Forces in Dielectric Continuum Theory of Solvation

Daniel M. Chipman
Radiation Laboratory
University of Notre Dame
Notre Dame, IN 46556

Dielectric continuum models are often used to simplify description of the intermolecular forces that govern the effects of a solvent on properties of a solute. Some interesting theoretical issues arise when coupling a classical dielectric continuum to a quantum mechanical solute. Unconstrained calculation of the solute electronic structure inevitably leads to a tail of the solute charge density that penetrates outside the cavity nominally enclosing it. For cavity sizes that are typically used in practice this penetration of solute electronic density into the solvent region is usually significant. It leads to a rarely recognized volume polarization of the dielectric that contributes in addition to the commonly treated surface polarization. We will show how this volume polarization arises in theory, an accurate computational method to treat it explicitly, a facile means to approximate it in terms of a certain additional surface polarization, and examples of when it has important effects on solute properties.