Nonlinear continuum model for solvated electronic structure

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Abstract

Density functional theory, coupled to a polarizable continuum model (PCM), can accurately describe electronic structure of molecules and metallic surfaces in a liquid. However, due to the linear reponse assumption in PCMs, it fails to be as successful when microscopic electric fields are strong. For example, this is the case when ions or ionic surfaces are solvated in a liquid. We formulate a nonlinear generalization of polarizable continuum models within the framework of joint density-functional theory, in which dielectric saturation effects, critical for highly polar systems, are included naturally. We also discuss applications of this theory to the calculation of electron enegy-loss and optical excitation spectrum of solvated ions.