Discrete Image Approximations of Ionic Solvent Induced Reaction Field to Charges

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Abstract. Two methods of discrete images are proposed to approximate the reaction field from ionic solvent for a point charge inside a dielectric spherical cavity. Fast and accurate calculation of such a reaction field is needed in hybrid explicit/implicit solvation models of biomolecules. A first- and a second-order image approximation methods, in the order of $u = \lambda a$ (λ – the inverse Debye screening length of the ionic solvent, a – the radius of the spherical cavity), are derived. Each method involves a point image at the conventional Kelvin image point and a line image along the ray from the Kelvin image point to infinity. Based on these results, discrete point images are obtained by using Jacobi-Gauss quadratures. Numerical results demonstrate that two to three point images are sufficient to achieve a 10^{-3} accuracy in the reaction field with the second-order image approximation.

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Key words: Method of images, reaction field, ionic solvent, hybrid solvation model.

1 Introduction

Solvent environment is well-known to provide a crucial contribution to the structure, dynamics and function of biological macromolecules. When modelling biological systems numerically, it has been challenging, however, to account for this environment in a manner that is computationally efficient and physically accurate at the same time. Explicit representation of solvent molecules [1–3] offers a detailed and accurate description of a biological macromolecule, yet the large number of atoms needed limits the size of the simulated system. Alternatively, implicit solvent models [4,5] reduce the solute-solvent

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interactions to their mean-field characteristics, expressed as a function of the solute configuration alone, and thus yield significant computational savings. However, these methods also have fundamental limitations due to the fact that the important atomic interaction at the solute-solvent interfaces is ignored. In order to take advantage of the efficiency of the implicit solvent models while also account for structural effects of the solvent in the proximity of the solute, hybrid explicit/implicit solvent models [6–8] have emerged as promising tools for biomolecular simulations. For example, the most common hybrid approach, the solvent shell method [9–12], typically employs explicit solvent only for the first few solvation shells of the solute, with a surrounding dielectric continuum to model bulk effects beyond the shells.

In this paper, we will extend our previous work [13] on discrete image approximations of the reaction field of a dielectric sphere in hybrid solvation models with the pure water solvent to the case of an ionic solvent. Spherical cavities are often used because the reaction field of a spherical dielectric can be solved analytically [12–18]. The main purpose for discrete image approximations to reaction fields is to apply the fast multipole methods directly [13, 19, 20] in calculating the electrostatic interactions among N charges inside the spherical cavity in $\mathcal{O}(N)$ operations.

For the pure water solvent, namely, with no ions present in the solvent, a variety of approaches exist for calculating the reaction field for charges inside the spherical cavity, including Kirkwood's classical series expansion [14], Friedman's image approximation [21], and Abagyan's modified image approximation (MIMEL) [22]. Applications of these image approximations in molecular dynamics or Monte Carlo simulations can be found in [23–27]. All these image approximation methods use only one image charge to represent the reaction field with limited accuracy. Recently, a high-order accurate, multiple image approximation [13] has been proposed based on a theoretical result of over 100 year history dating back to 1883 by C. Neumann [28], which extended the conventional Kelvin image [29] for a conducting sphere to the case of a dielectric one. In the case of a dielectric sphere, an image point charge at the Kelvin image point together with an image line charge along a ray from the Kelvin image point to infinity can be used to represent the reaction field exactly. Lindell and Norris [30–33] have provided the power law distribution for the image line charge density along the ray in 1990s. The high-order accurate, multiple discrete image approximation to the reaction field was then obtained by representing the image line charge with an equivalent set of discrete point charges constructed by using Jacobi-Gauss quadratures [13].

For an ionic solvent, the treatment of charge density due to ions in solution needs special consideration. If we assume that the mobile charge concentrations are given by the Debye-Hückel theory, for a solvent of weak ionic strength the linearized Poisson-Boltzmann equation [34–38] can be used to model the potential field in the solvent. In the case of a spherical cavity, analytical solution of the linearized Poisson-Boltzmann equation goes back to the work published by Kirkwood [14, 17]. Utilizing Kirkwood's basic idea, Alper and Levy proposed a so-called generalized reaction field method for molecular dynamics simulations of liquid water [39]. Although they introduced one or