

Image Methods for Electrostatic Potentials

Wei Cai

Department of Mathematics and Statistics
University of North Carolina at Charlotte
Charlotte, NC 28223-0001, USA

Abstract

Image method is a classical method for finding electrostatic potentials in dielectric or conducting objects with special geometries. The image method provides simple and analytical formulas to represent the reaction field on a charge in an object as a result of the polarization effect from the surrounding material. In this paper, we will provide an overview of the classical results of image methods for electrostatic potentials in simple geometries, and recent developments in constructing image approximations for reaction fields in a dielectric sphere.

1 Introduction

Electrostatics plays a major role in many physical problems such as electromagnetic wave propagation, structure and folding and stability of proteins. In the case of biomolecule simulations, the long range electrostatic interactions strongly depend on the solvent environment surrounding the biomolecule under study. When modeling a biological system numerically, it has been challenging, however, to account for such environment in a manner that is computationally efficient and physically accurate at the same time. As such, theoretical modeling of electrostatic interactions has been and remains an important subject of theoretical and computational studies of biomolecules.

One of the fundamental problems in electrostatics is to find the potential distribution of a single charge in a heterogeneous medium, for instance, a charge embedded in a cavity of one dielectric constant surrounded/adjacent to another medium with a different dielectric constant. A classic example for this setting is to find the solvation energy of a water molecule in the infinite solvent environment, which was first studied by Born in [3] with the Born solvation energy formula. More recently, in efforts to speed up the computational modeling of the solvation of macromolecules, hybrid models of representation

[31, 23, 22] of the biomolecule and solvent is being studied to take advantage of the accuracy of explicit atomic models [21, 24, 34] of the biomolecules and water shells on one hand, and the speed of implicit models [10, 2] using continuum dielectric representations for the infinite extent of solvent away from the biomolecules on the other hand. In the hybrid model, a spherical or elliptic cavity is usually used to enclose the biomolecule and some solvent molecules. The key physical quantity for molecular dynamics simulation of the molecules inside the cavity is to calculate the reaction field of charges from the infinite extent of continuum dielectric solvent (pure water or ionic solvent).

Electric charges within the cavity will polarize the surrounding solvent medium, which in turn makes a contribution, called the reaction field, to the electric potential within the cavity. The electric potential inside the cavity is expressed as $\Phi = \Phi_s + \Phi_{\text{RF}}$ where Φ_s is the potential from the source charge inside the cavity, and Φ_{RF} is the reaction field. Fast and accurate calculation of such a reaction field has a far-reaching impact on computational simulations for chemical and biological systems involving electrostatic interactions within a solvent. In the case of a spherical cavity, the reaction field can be calculated using the classical Kirkwood series expansion [19, 20]. Although in theory any desired degree of accuracy can be obtained using the series expansion, its convergence rate is slow near the cavity boundary.

For some cavity geometries, classical image methods [26] provide simple and analytic ways to compute the reaction fields. As computational modeling of biological systems has gained increasing prominence for the study of proteins and membrane, research on image methods for dielectric materials have attracted more attentions. For this reason, several image charge approaches have been proposed in which the reaction field for a dielectric sphere is represented in terms of the potential of a single image charge, including the Friedman image approximation [13] and the Abagyan-Totrov modified image approximation [1]. However, by using only one image charge these methods were limited in accuracy. Recently, a high-order accurate approximation using multiple image charges was proposed [4, 8, 9] which was found to perform about 20-30 times faster than the Kirkwood expansion in typical high accuracy calculations. Moreover, combined with the fast multipole methods [16, 15], the multiple image approximation has the potential to calculate electrostatic interactions among N charges inside the spherical cavity in $O(N)$ operations.

In this paper, we will provide an overview of the traditional results of image methods for electrostatic potentials in simple geometries, and the recent development alluded above in constructing image approximations for reaction fields of a dielectric sphere. For image methods applied to multiple objects

such as cylinders and spheres, please refer to [36, 18, 38, 6, 5].

2 Method of Images for Simple Geometries

Let Ω be the region where the electrostatic potential $\Phi(r)$, due to the presence of a source charge q located at \mathbf{r}_s inside Ω , will be found and the potential will satisfy the Poisson equation

$$\nabla \cdot (\epsilon(\mathbf{r})\nabla\Phi(\mathbf{r})) = -4\pi q\delta(|\mathbf{r} - \mathbf{r}_s|), \quad \mathbf{r} \in \Omega \quad (1)$$

where the potential will satisfy a homogeneous boundary conditions if Ω^c is a perfect conductor

$$\Phi(\mathbf{r}) = 0, \quad \mathbf{r} \in \partial\Omega \quad (2)$$

or the continuity condition if both Ω and Ω^c (the exterior of Ω) are dielectric material,

$$\begin{aligned} \Phi(\mathbf{r}^+) &= \Phi(\mathbf{r}^-), \\ \epsilon_o \frac{\partial\Phi(\mathbf{r}^+)}{\partial n} &= \epsilon_i \frac{\partial\Phi(\mathbf{r}^-)}{\partial n} \end{aligned} \quad (3)$$

where n is the external normal to the boundary, and ϵ_i is the dielectric constant inside Ω and ϵ_o the dielectric constant outside Ω (namely in Ω^c) and $+$ and $-$ denotes the limit taking from outside and inside Ω , respectively. Meanwhile, the potential $\Phi(\mathbf{r})$ is assumed to decay to zero when $\mathbf{r} \rightarrow \infty$.

In general, the solution to (1) has to be solved with numerical approximation, and analytical forms of the solutions are only available for simple geometries. The solution for the total potential $\Phi(\mathbf{r})$ is usually decomposed into two parts - one part for the potential due to the source charge at \mathbf{r}_s and the second part the reaction field which represents the polarization effect of the material in Ω^c , namely,

$$\Phi(\mathbf{r}) = \frac{q}{4\pi\epsilon_i|\mathbf{r} - \mathbf{r}_s|} + \Phi_{\text{RF}}(\mathbf{r}). \quad (4)$$

For selected geometries, the method of images provide simple and analytical solutions to the reaction field $\Phi_{\text{RF}}(\mathbf{r})$. In this section, we will review some classic image solutions to simple geometries of conducting bodies and dielectrics.

For simplicity of presentation, we will introduce the following notations

$$\kappa = \frac{\epsilon_o}{\epsilon_i}, \quad \Gamma = \frac{\epsilon_o - \epsilon_i}{\epsilon_o + \epsilon_i} = \frac{\kappa - 1}{\kappa + 1}, \quad \Upsilon = \frac{2\epsilon_o}{\epsilon_o + \epsilon_i} \quad (5)$$

and the potential at \mathbf{r} due to a point charge q located in \mathbf{r}_s in a homogeneous free space with dielectric constant ϵ is denoted by

$$U[q, \mathbf{r}_s, \epsilon] = U[q, \mathbf{r}_s, \epsilon](\mathbf{r}) = -\frac{q}{2\pi\epsilon} \ln(|\mathbf{r} - \mathbf{r}_s|) \quad \mathbf{r} = (x, y) \in R^2, \quad (6)$$

or

$$V[q, \mathbf{r}_s, \epsilon] = V[q, \mathbf{r}_s, \epsilon](\mathbf{r}) = \frac{q}{4\pi\epsilon|\mathbf{r} - \mathbf{r}_s|} \quad \mathbf{r} = (x, y, z) \in R^3 \quad (7)$$

with the argument \mathbf{r} omitted in most cases when no confusion occurs.

2.1 Potential of a point charge in the presence of a conducting 3-D half space

Consider a point charge located at $\mathbf{r}_s = (0, 0, d)$ along the z -axis above a conducting plane which is assumed to be grounded (at zero potential). So, we have $\Omega = \{\mathbf{r} = (x, y, z), z \geq 0\}$ and the homogeneous boundary condition (2) is assumed. The solution to (1) is given by (4). And, the reaction field in this case can in fact be represented by the field of an image charge $q' = -q$ which is located below the conducting plane $z = 0$ at the mirror image location $\mathbf{r}_{im} = (0, 0, -d)$ and the effect of this image potential (reaction potential) is to satisfy the required zero potential boundary conditions (2). So, we have

$$\Phi_{\text{RF}}(\mathbf{r}) = -\frac{q}{4\pi\epsilon_i|\mathbf{r} - \mathbf{r}_{im}|} = V[-q, \mathbf{r}_{im}, \epsilon_i]. \quad (8)$$

2.2 Potential of a point charge in the presence of a dielectric 3-D half space

Again, we have a point charge located at $\mathbf{r}_s = (0, 0, d)$ above a dielectric half space and the potential in Ω will have to satisfy the continuity conditions (3) on the interface $z = 0$. Again the potential is given by (4). The reaction field can be represented by an image charge, specifically, for $z > 0$, we have

$$\Phi_{\text{RF}}(\mathbf{r}) = V[q', \mathbf{r}_{im}, \epsilon_i] \quad (9)$$

where

$$\mathbf{r}_{im} = (0, 0, -d), \quad q' = -\Gamma q.$$

Meanwhile, the total potential in the lower half plane can also be represented by a second image locating at the source point in the upper half plane - consistent with the non-singular feature of the potential there, i.e., for $z < 0$,

$$\Phi(\mathbf{r}) = V[q'', \mathbf{r}_s, \epsilon_o] \quad (10)$$

where

$$q'' = \frac{2\epsilon_o}{(\epsilon_o + \epsilon_i)} q.$$

2.3 Potential of a line charge and a dielectric cylinder

In this case, the problem is a 2-D problem for the cross section of the cylinder, let $\Omega = \{\mathbf{r} = (r, \theta), r > a\}$ denote the exterior of the cylinder of radius a which contains a source charge q at location $\mathbf{r}_s = (r_s, \theta_s = 0)$, $r_s > a$ in the polar coordinates.

The potential inside Ω is the superposition of the potential from the source charge and two images at 0 and $\mathbf{r}_{im} = (\frac{a^2}{r_s}, 0)$, [37] i.e.

$$\Phi(\mathbf{r}) = U[q, \mathbf{r}_s, \epsilon_i] + U[-q, 0, \epsilon_i] + U[q', \mathbf{r}_{im}, \epsilon_i], \quad |\mathbf{r}| > a \quad (11)$$

where

$$q' = -\Gamma q.$$

while the potential outside Ω (inside the cylinder) is given by a second image q'' at location r_s

$$\Phi(\mathbf{r}) = U[q'', \mathbf{r}_s, \epsilon_o], \quad |\mathbf{r}| < a \quad (12)$$

where $q'' = \Upsilon q$.

2.4 Potential of a line charge and a conducting cylinder

As a limiting case of (11), we can find the potential outside the cylinder centered at origin due to a line charge placed at $(r_s, \theta_s = 0)$, $r_s > a$ as

$$\Phi(\mathbf{r}) = U[q, \mathbf{r}_s, \epsilon_i] + U[q', \mathbf{r}_{im}, \epsilon_i], \quad |\mathbf{r}| > a \quad (13)$$

where $q' = -q$, $\mathbf{r}_{im} = (\frac{a^2}{r_s}, 0)$.

2.5 Potential of a line charge in a 3-D wedge of angle π/m with conducting boundary

Let $\Omega = \{(r, \theta), -\frac{\pi}{2m} \leq \theta \leq \frac{\pi}{2m}, r > 0\}$ be a dielectric wedge with dielectric constant ϵ_i with a conducting boundary and a line charge is placed at (r_s, θ_s) $-\frac{\pi}{2m} < \theta_s < \frac{\pi}{2m}, r_s > 0$. The potential inside the wedge Ω can be found [37] by m charges, including the source charge and $(m - 1)$ image charges, with charge q and, m image charges with charge $-q$, namely,

$$\Phi(\mathbf{r}) = \sum_{i=1}^m U[q, (r_s, \theta_s + i\frac{2\pi}{m}), \epsilon_i] + \sum_{i=1}^m U[-q, (r_s, -\theta_s + i\frac{2\pi}{m}), \epsilon_i] \quad (14)$$

2.6 Potential of a point charge in a 3-D dielectric wedge

Nikoskinen and Lindel [29] proposed an ingenious image method to find the potential due to a point charge outside a dielectric wedge $W = \{ \mathbf{r} = (\rho, \varphi, z) | -\Theta < \varphi < \Theta \}$ of dielectric constant ϵ_o in cylindrical coordinates. So in this case, our domain $\Omega = W^c = \{ \mathbf{r} = (\rho, \varphi, z) | \Theta < \varphi < 2\pi - \Theta \}$ which will have a dielectric constant ϵ_i . The potential due to a charge q located at $\mathbf{r}_s = (\rho_s, \varphi_s, z_s) \in \Omega$ can be expressed using discrete images and surface image density at both real physical and complex locations as follows.

The potential inside Ω (outside the wedge)

$$\begin{aligned} \Phi(\mathbf{r}) = & V[q, (\rho_s, \varphi_s, z_s), \epsilon_i] + \sum_{n=1}^N V[q(-\Gamma)^n, (\rho_s, \alpha_n^e, z_s), \epsilon_i] \\ & + \sum_{m=1}^M V[q(-\Gamma)^m, (\rho_s, \beta_m^e, z_s), \epsilon_i], \\ & + \int_{-i\infty}^{i\infty} V[q_e(\zeta), (\rho_s, \zeta, z_s), \epsilon_i] d\zeta \quad (\rho, \varphi, z) \in \Omega \end{aligned} \quad (15)$$

where the first term is from the source charge and the second summation is from $N = \text{integer}[\frac{2\pi - \varphi_s}{2(\pi - \Theta)}]$ discrete image charges of $q(-\Gamma)^n$ located at

$$(\rho_s, \alpha_n^e, z_s), \quad \alpha_n^e = (-1)^n [2n(\pi - \Theta) + \varphi_s - 2\pi]$$

and $M = \text{integer}[\frac{\varphi_s}{2(\pi - \Theta)}]$ discrete image charges of $q(-\Gamma)^m$ located at

$$(\rho_s, \beta_m^e, z_s), \quad \beta_m^e = (-1)^m [\varphi_s - 2m(\pi - \Theta)]$$

and a line image of density $q_e(\zeta)$ distributed along the imaginary location $(\rho_s, \zeta, z_s), \zeta \in (-i\infty, i\infty)$ and

$$q_e(\zeta) = q_e(ip) = -\frac{iq}{2\pi} \int_{-\infty}^{\infty} [q_{ee}(t) + q_{eo}(t)] e^{-itp} dt$$

where

$$\begin{aligned} q_{eo}(t) = & \frac{-\Gamma \sinh(2t\Theta) \sinh[t(\pi - \varphi_s)]}{\sinh(t\pi) + \Gamma \sinh[t(\pi - 2\Theta)]} - \sum_{n=1}^N (-\Gamma)^n \sinh(t\alpha_n^e) - \sum_{m=1}^M (-\Gamma)^m \sinh(t\beta_m^e) \\ q_{ee}(t) = & \frac{-\Gamma \sinh(2t\Theta) \cosh[t(\pi - \varphi_s)]}{\sinh(t\pi) - \Gamma \sinh[t(\pi - 2\Theta)]} - \sum_{n=1}^N (-\Gamma)^n \cosh(t\alpha_n^e) - \sum_{m=1}^M (-\Gamma)^m \cosh(t\beta_m^e). \end{aligned}$$

Similarly, the potential outside Ω (inside the wedge)

$$\begin{aligned}
\Phi(\mathbf{r}) = & \Upsilon(V[q, (\rho_s, \varphi_s, z_s), \epsilon_o] + \sum_{n=1}^N V[q\Gamma^n, (\rho_s, \alpha_n^i, z_s), \epsilon_o] \\
& + \sum_{m=1}^M V[q\Gamma^m, (\rho_s, \beta_m^i, z_s), \epsilon_o] \\
& + \int_{\pi-i\infty}^{\pi+i\infty} V[q_i(\zeta), (\rho_s, \zeta, z_s), \epsilon_o] d\zeta.
\end{aligned} \tag{16}$$

The first term in (16) is from an image charge q located at (ρ_s, φ_s, z_s) and the second summation is from $N = \text{integer}[\frac{\pi-\varphi_s}{2\Theta}]$ discrete image charges of $q\Gamma^n$ located at

$$(\rho_s, \alpha_n^e, z_s), \alpha_n^i = \pi + (-1)^n[\varphi_s - \pi + 2n\Theta]$$

and $M = \text{integer}[\frac{\varphi_s-\pi}{2\Theta}]$ discrete image charges of $q\Gamma^m$ located at

$$(\rho_s, \beta_n^i, z_s), \beta_n^e = \pi + (-1)^m[\varphi_s - \pi - 2m\Theta]$$

and a line image of density $q_e(\zeta)$ distributed along the imaginary location $(\rho_s, \zeta, z_s), \zeta \in (-i\infty, i\infty)$ and

$$q_i(\zeta) = q_i(\pi - ip) = -\frac{iq}{2\pi} \int_{-\infty}^{\infty} [q_{ie}(t) + q_{io}(t)] e^{-itp} dt$$

where

$$\begin{aligned}
q_{io}(t) = & \frac{\sinh[t(\pi - \varphi_s)]}{\sinh(t\pi) + \Gamma \sinh[t(\pi - 2\Theta)]} - \sinh[t(\pi - \varphi_s)] \\
& - \sum_{n=1}^N \Gamma^n \sinh[t(\pi - \alpha_n^i)] - \sum_{m=1}^M \Gamma^m \sinh[t(\pi - \beta_m^i)],
\end{aligned}$$

$$\begin{aligned}
q_{ie}(t) = & \frac{\cosh[t(\pi - \varphi_s)]}{\sinh(t\pi) - \Gamma \sinh[t(\pi - 2\Theta)]} - \cosh[t(\pi - \varphi_s)] \\
& - \sum_{n=1}^N \Gamma^n \cosh[t(\pi - \alpha_n^i)] - \sum_{m=1}^M \Gamma^m \cosh[t(\pi - \beta_m^i)].
\end{aligned}$$

2.7 Potential of a point charge in the presence of a conducting sphere

For a charge q outside a conducting sphere, i.e $\Omega = \{\mathbf{r}, |\mathbf{r}| > \mathbf{a}\}$ and the potential in Ω will be given as the sum of the primary field at $\mathbf{r}_s = (r_s, \theta_s, \phi_s)$ in the spherical coordinates and the potential of an image charge $-q$ at the Kelvin image (1885) which is the inversion point $\mathbf{r}_k = (\frac{a^2}{r_s}, \theta_s, \phi_s)$ with respect to the sphere,

$$\Phi(\mathbf{r}) = V[q, \mathbf{r}_s, \epsilon_i] + V[-q, \mathbf{r}_k, \epsilon_i], \quad \mathbf{r} \in \Omega. \quad (17)$$

2.8 Potential of a point charge in the presence of a dielectric sphere

In this case, we consider the sphere $\Omega = \{\mathbf{r}, |\mathbf{r}| \leq \mathbf{a}\}$ with a charge q located at $\mathbf{r}_s = (r_s, \theta_s, \phi_s) \in \Omega$, the potential inside and outside the sphere can be approximated by those of a point charge at the Kelvin image location and a line image charges with a power law distribution density along a ray extending from the Kelvin image point $\mathbf{r}_k = (\frac{a^2}{r_s}, \theta_s, \phi_s)$ to infinity (for the reaction field inside the sphere) or along a ray between the origin and the Kelvin point (for reaction field outside the sphere if the source charge is outside the sphere). This representation has been discovered by several authors independently. However, it is still not well known in the electrostatic research communities. The earliest such a result was obtained by C. Neumann [28] in 1883, and, then by Finkelstein [11] in 1977, and later rediscovered in the 1990s independently by Lindell and Norris [25, 30]. The result shows that the reaction field inside the sphere

$$\begin{aligned} \Phi_{\text{RF}}(\mathbf{r}) &= \frac{q_k}{4\pi\epsilon_i|\mathbf{r} - \mathbf{r}_k|} + \int_{r_k}^{\infty} \frac{q'(x)}{4\pi\epsilon_i|\mathbf{r} - \mathbf{x}|} dx \\ &= V[q_k, \mathbf{r}_k, \epsilon_i] + \int_{r_k}^{\infty} V[q'(x), \mathbf{x}, \epsilon_i] dx, \quad \mathbf{r} \in \Omega. \end{aligned} \quad (18)$$

where $\mathbf{x} = x \frac{\mathbf{r}_s}{r_s}$, $r_k = \frac{a^2}{r_s}$

$$q_k = -\Gamma \frac{a}{r_s} q, \quad q'(x) = \frac{\epsilon_i(\epsilon_i - \epsilon_o)}{(\epsilon_i + \epsilon_o)^2} \frac{q}{a} \left(\frac{r_k}{x}\right)^{\epsilon_o/(\epsilon_i + \epsilon_o)}, \quad r_k \leq x.$$

Meanwhile, the total potential outside the sphere is given by a point image charge at \mathbf{r}_s and a line charge distributing along the ray from origin to \mathbf{r}_s , i.e.

$$\begin{aligned}\Phi(\mathbf{r}) &= \frac{q_s''}{4\pi\epsilon_o|\mathbf{r}-\mathbf{r}_s|} + \int_0^{r_s} \frac{q''(x)}{4\pi\epsilon_o|\mathbf{r}-\mathbf{x}|} dx \\ &= V[q_s'', \mathbf{r}_s, \epsilon_o] + \int_0^{r_s} V[q''(x), \mathbf{x}, \epsilon_o] dx,\end{aligned}\quad (19)$$

where

$$q_s'' = \Upsilon q, \quad q''(x) = -\frac{q}{r_s} \frac{\Gamma\Upsilon}{2} \left(\frac{x}{r_s}\right)^{-\epsilon_i/(\epsilon_i+\epsilon_o)}, \quad 0 \leq x \leq r_s.$$

3 The Discrete Image Approximations for Reaction Fields in a Dielectric Sphere

In this section, we will present the recent development of constructing discrete image approximations to the reaction field for a dielectric sphere $\Omega = \{\mathbf{r}, |\mathbf{r}| < a\}$ with dielectric constant ϵ_i while the dielectric constant outside the sphere is assumed to be ϵ_o . The starting point of most of the results is the classical series expansion due to Kirkwood (Kirkwood series expansion) [19] for the reaction fields. The recent results on multiple image approximations are based on the elegant line image formula in (18) through appropriate Gauss integration. Also, extension to the Poisson-Boltzmann equation is also included when the medium outside the sphere has an ionic density.

3.1 The Kirkwood series expansion of reaction field for a dielectric sphere

For a charge q inside a dielectric sphere Ω and the potential is the solution of (1) and (3) for Ω , which is given by (4) and the reaction field $\Phi_{\text{RF}}(\mathbf{r})$ at an observation point $\mathbf{r}=(r, \theta, \phi)$ inside the sphere can be expressed in terms of the Legendre polynomials of $\cos \theta$ [19], namely,

$$\Phi_{\text{RF}}(\mathbf{r}) = \frac{q(\epsilon_i - \epsilon_o)}{4\pi\epsilon_i a} \sum_{n=0}^{\infty} \left(\frac{n+1}{\epsilon_i n + \epsilon_o(n+1)} \right) \left(\frac{r r_s}{a^2} \right)^n P_n(\cos \theta), \quad (20)$$

where $P_n(x)$, $n = 0, 1, 2, \dots$, are the Legendre polynomials.

The expansion in (20) is termed as the Kirkwood expansion, which has a fast convergence when r is away from the sphere boundary. In the case that the point charge is close to the boundary of the sphere, when calculating the reaction field at a point also close to the boundary, the convergence rate by the

Kirkwood series expansion is slow due to $rr_s/a^2 \approx 1$, requiring a great number of terms in the series expansion to achieve good accuracy in the reaction field.

3.2 The Kirkwood image approximation

Assume that $\epsilon_i < \epsilon_o$. Then expanding the term $(n+1)/(\epsilon_i n + \epsilon_o(n+1))$ in (20) in terms of $\epsilon_i n / \epsilon_o(n+1) < 1$ yields

$$\frac{n+1}{\epsilon_i n + \epsilon_o(n+1)} = \frac{1}{\epsilon_o} \left[1 - \frac{\epsilon_i}{\epsilon_o} \frac{n}{n+1} + \left(\frac{\epsilon_i}{\epsilon_o} \right)^2 \left(\frac{n}{n+1} \right)^2 - \dots \right],$$

which enables us to write the reaction field given in (20) as

$$\Phi_{\text{RF}}(\mathbf{r}) = B^{(0)}(\mathbf{r}) + B^{(1)}(\mathbf{r}) + B^{(2)}(\mathbf{r}) + \dots, \quad (21)$$

where for $k=0, 1, 2, \dots$, we have

$$B^{(k)}(\mathbf{r}) = (-1)^k \frac{(\epsilon_i - \epsilon_o)}{4\pi\epsilon_i\epsilon_o} \frac{a}{r_s} \frac{q}{(a^2/r_s)} \left(\frac{\epsilon_i}{\epsilon_o} \right)^k \sum_{n=0}^{\infty} \left(\frac{n}{n+1} \right)^k \left(\frac{r}{a^2/r_s} \right)^n P_n(\cos \theta).$$

In particular, the first term in (21) is

$$B^{(0)}(\mathbf{r}) = \frac{(\epsilon_i - \epsilon_o)}{4\pi\epsilon_i\epsilon_o} \frac{a}{r_s} \frac{q}{(a^2/r_s)} \sum_{n=0}^{\infty} \left(\frac{r}{a^2/r_s} \right)^n P_n(\cos \theta), \quad (22)$$

which is exactly the Legendre polynomial expansion of the Coulomb potential at the point \mathbf{r} inside the sphere due to a point charge of strength q_K outside the sphere at the conventional Kelvin image point $\mathbf{r}_k=(r_k, 0, 0)$ [27], namely,

$$B^{(0)}(\mathbf{r}) = \frac{q_K}{4\pi\epsilon_i|\mathbf{r} - \mathbf{r}_k|} = V[q_K, \mathbf{r}_k, \epsilon_i],$$

where

$$q_K = \frac{\epsilon_i - \epsilon_o}{\epsilon_o} \frac{a}{r_s} q, \quad r_k = \frac{a^2}{r_s}.$$

The Kirkwood image approximation to the reaction field is then defined as

$$\Phi_{\text{RF}}(\mathbf{r}) \approx \hat{\Phi}_K(\mathbf{r}) = B^{(0)}(\mathbf{r}). \quad (23)$$

Now let us consider the second term in (21) which can be written as

$$\begin{aligned} B^{(1)}(\mathbf{r}) = & - \frac{(\epsilon_i - \epsilon_o)}{4\pi\epsilon_i\epsilon_o} \frac{a}{r_s} \frac{q}{(a^2/r_s)} \left(\frac{\epsilon_i}{\epsilon_o} \right) \sum_{n=0}^{\infty} \left(\frac{r}{a^2/r_s} \right)^n P_n(\cos \theta), \\ & + \frac{(\epsilon_i - \epsilon_o)}{4\pi\epsilon_i\epsilon_o} \frac{a}{r_s} \frac{q}{(a^2/r_s)} \left(\frac{\epsilon_i}{\epsilon_o} \right) \sum_{n=0}^{\infty} \left(\frac{1}{n+1} \right) \left(\frac{r}{a^2/r_s} \right)^n P_n(\cos \theta). \end{aligned} \quad (24)$$

Similarly, the first series in (24) is exactly the Legendre polynomial expansion of the Coulomb potential at the point \mathbf{r} inside the sphere due to a point charge of strength q'_K outside the sphere at the Kelvin image point \mathbf{r}_K , where

$$q'_K = -\frac{\epsilon_i(\epsilon_i - \epsilon_o)}{\epsilon_o^2} \frac{a}{r_s} q.$$

On the other hand, using the integral identity

$$\frac{1}{n+1} = r_K^{n+1} \int_{r_K}^{\infty} \frac{1}{x^{n+2}} dx, \quad (25)$$

which is valid for all $n \geq 0$, the second series in (24) can be written as

$$\int_{r_K}^{\infty} \left[\frac{\bar{q}_K(x)}{4\pi\epsilon_i x} \sum_{n=0}^{\infty} \left(\frac{r}{x}\right)^n P_n(\cos\theta) \right] dx, \quad (26)$$

where

$$\bar{q}_K(x) = \frac{\epsilon_i(\epsilon_i - \epsilon_o)}{\epsilon_o^2} \frac{q}{a} \left(\frac{r_K}{x}\right), \quad r_K \leq x.$$

Note that $\bar{q}_K(x)$ can be regarded as the density function of a continuous line charge extending along the radial direction from the Kelvin image point \mathbf{r}_K to infinity. Also, the integrand in (26) is exactly the Legendre polynomial expansion of the Coulomb potential at the point \mathbf{r} inside the sphere due to a charge of strength $\bar{q}_K(x)$ outside the sphere at the point $\mathbf{x}=(x, 0, 0)$. Hence we get

$$B^{(1)}(\mathbf{r}) = \frac{q'_K}{4\pi\epsilon_i|\mathbf{r} - \mathbf{r}_K|} + \int_{r_K}^{\infty} \frac{\bar{q}_K(x)}{4\pi\epsilon_i|\mathbf{r} - \mathbf{x}|} dx.$$

The Kirkwood image approximation (23) can then be improved by including $B^{(1)}(\mathbf{r})$ as a correction potential, and the resulting image approximation is referred to by us as the improved Kirkwood image approximation, namely,

$$\begin{aligned} \Phi_{\text{RF}}(\mathbf{r}) &\approx \hat{\Phi}_{\text{IK}}(\mathbf{r}) = B^{(0)}(\mathbf{r}) + B^{(1)}(\mathbf{r}) = \frac{q_{\text{IK}}}{4\pi\epsilon_i|\mathbf{r} - \mathbf{r}_K|} + \int_{r_K}^{\infty} \frac{\bar{q}_K(x)}{4\pi\epsilon_i|\mathbf{r} - \mathbf{x}|} dx \\ &= V[q_{\text{IK}}, \mathbf{r}_K, \epsilon_i] + \int_{r_K}^{\infty} V[\bar{q}_K(x), \mathbf{x}, \epsilon_i] dx, \end{aligned} \quad (27)$$

where

$$q_{\text{IK}} = q_K + q'_K = -\frac{(\epsilon_i - \epsilon_o)^2}{\epsilon_o^2} \frac{a}{r_s} q.$$

Furthermore, by evaluating the integral in (27) explicitly, a compact analytical form of the improved Kirkwood image approximation can be obtained as

$$\hat{\Phi}_{\text{IK}}(\mathbf{r}) = \frac{q_{\text{IK}}}{4\pi\epsilon_i|\mathbf{r} - \mathbf{r}_k|} + \begin{cases} \frac{\epsilon_i - \epsilon_o}{4\pi\epsilon_o^2} \frac{q}{a\xi} \ln\left(\frac{\sqrt{1 - 2\cos\theta\xi + \xi^2} + \xi - \cos\theta}{1 - \cos\theta}\right), & \text{if } \cos\theta \neq 1, \\ -\frac{\epsilon_i - \epsilon_o}{4\pi\epsilon_o^2} \frac{q}{a\xi} \ln(1 - \xi), & \text{if } \cos\theta = 1, \end{cases}$$

where $\xi = rr_s/a^2$.

3.3 The Friedman image approximation

Alternatively, expanding the term $(n+1)/(\epsilon_i n + \epsilon_o(n+1))$ in (20) in terms of $\epsilon_i/((\epsilon_i + \epsilon_o)(n+1)) < 1$ results in

$$\frac{n+1}{\epsilon_i n + \epsilon_o(n+1)} = \frac{1}{\epsilon_i + \epsilon_o} \left[1 + \frac{\epsilon_i}{\epsilon_i + \epsilon_o} \frac{1}{n+1} + \left(\frac{\epsilon_i}{\epsilon_i + \epsilon_o}\right)^2 \left(\frac{1}{n+1}\right)^2 + \dots \right], \quad (28)$$

which enables us to write the reaction field given in (20) as

$$\Phi_{\text{RF}}(\mathbf{r}) = R^{(0)}(\mathbf{r}) + R^{(1)}(\mathbf{r}) + R^{(2)}(\mathbf{r}) + \dots, \quad (29)$$

where for $k=0, 1, 2, \dots$, we have

$$R^{(k)}(\mathbf{r}) = \frac{(\epsilon_i - \epsilon_o)\epsilon_i^k}{4\pi\epsilon_i(\epsilon_i + \epsilon_o)^{k+1}} \frac{a}{r_s} \frac{q}{(a^2/r_s)} \sum_{n=0}^{\infty} \left(\frac{1}{n+1}\right)^k \left(\frac{r}{a^2/r_s}\right)^n P_n(\cos\theta). \quad (30)$$

In particular, the first term in (29) is

$$R^{(0)}(\mathbf{r}) = \frac{\epsilon_i - \epsilon_o}{4\pi\epsilon_i(\epsilon_i + \epsilon_o)} \frac{a}{r_s} \frac{q}{(a^2/r_s)} \sum_{n=0}^{\infty} \left(\frac{r}{a^2/r_s}\right)^n P_n(\cos\theta),$$

which is the Legendre polynomial expansion of the Coulomb potential at the point \mathbf{r} inside the sphere due to a point charge of strength q_F outside the sphere at the Kelvin image point \mathbf{r}_k , namely,

$$R^{(0)}(\mathbf{r}) = \frac{q_F}{4\pi\epsilon_i|\mathbf{r} - \mathbf{r}_k|} = V[q_F, \mathbf{r}_k, \epsilon_i],$$

where

$$q_F = -\Gamma \frac{a}{r_s} q.$$

The Friedman image approximation to the reaction field [13] is thus defined as

$$\Phi_{\text{RF}}(\mathbf{r}) \approx \hat{\Phi}_{\text{F}}(\mathbf{r}) = R^{(0)}(\mathbf{r}). \quad (31)$$

Next, let us consider the second term in (29) which is

$$R^{(1)}(\mathbf{r}) = \frac{(\epsilon_i - \epsilon_o)\epsilon_i}{4\pi\epsilon_i(\epsilon_i + \epsilon_o)^2} \frac{a}{r_s} \frac{q}{(a^2/r_s)} \sum_{n=0}^{\infty} \left(\frac{1}{n+1} \right) \left(\frac{r}{a^2/r_s} \right)^n P_n(\cos\theta).$$

Using the integral identity (25) again, $R^{(1)}(\mathbf{r})$ can be regarded as the potential of a continuous line charge extending along the radial direction from the Kelvin image point \mathbf{r}_k to infinity with the charge density function given by

$$\bar{q}_{\text{F}}(x) = \frac{\epsilon_i(\epsilon_i - \epsilon_o)}{(\epsilon_i + \epsilon_o)^2} \frac{q}{a} \left(\frac{r_k}{x} \right), \quad r_k \leq x,$$

namely,

$$R^{(1)}(\mathbf{r}) = \int_{r_k}^{\infty} \frac{\bar{q}_{\text{F}}(x)}{4\pi\epsilon_i|\mathbf{r} - \mathbf{x}|} dx = \int_{r_k}^{\infty} V[\bar{q}_{\text{F}}(x), \mathbf{x}, \epsilon_i] dx. \quad (32)$$

Note that the line charge $\bar{q}_{\text{F}}(x)$ is a constant multiple of the line charge $\bar{q}_{\text{K}}(x)$.

Also, integrating (32) leads to a compact analytical form for $R^{(1)}(\mathbf{r})$ as

$$R^{(1)}(\mathbf{r}) = \begin{cases} \frac{\epsilon_i - \epsilon_o}{4\pi(\epsilon_i + \epsilon_o)^2} \frac{q}{a\xi} \ln \left(\frac{\sqrt{1 - 2\cos\theta\xi + \xi^2} + \xi - \cos\theta}{1 - \cos\theta} \right), & \text{if } \cos\theta \neq 1, \\ -\frac{\epsilon_i - \epsilon_o}{4\pi(\epsilon_i + \epsilon_o)^2} \frac{q}{a\xi} \ln(1 - \xi), & \text{if } \cos\theta = 1. \end{cases}$$

Consequently, the Friedman image approximation can be improved by including $R^{(1)}(\mathbf{r})$ as a correction potential, and the resulting image approximation is referred to by us as the improved Friedman image approximation, namely,

$$\Phi_{\text{RF}}(\mathbf{r}) \approx \hat{\Phi}_{\text{IF}}(\mathbf{r}) = R^{(0)}(\mathbf{r}) + R^{(1)}(\mathbf{r}). \quad (33)$$

The Friedman image approximation has been applied in many areas including molecular dynamics or Monte Carlo simulations [39, 40, 33]. From (28) and (30), we can see that the accuracy of the improved Friedman image approximation is limited to the second order of the dielectric constant contrast, i.e. $\left(\frac{\epsilon_i}{\epsilon_i + \epsilon_o} \right)^2$. On the other hand, it is clear from (30) that the approximation holds even when the source charge r_s approaches to the sphere boundary.

3.4 The Abagyan-Totrov image approximation

The Friedman image approximation (31) or (33) provides insufficient accuracy. In particular, when r_s tends to zero so that the point charge is located in the center of the sphere, the reaction field energy based on the Friedman image approximation (31) does not reproduce the Born formula [1].

Based on the Friedman image approximation (31), Abagyan and Totrov proposed a modified image approximation which is more accurate and less computationally intensive than the improved Friedman image approximation (33). Instead of an exact expression for $R^{(1)}(\mathbf{r})$, a position-independent correction potential R^{corr} is added to the Friedman image approximation (31) so that for the particular case of a charge in the center of the sphere one gets the exact solution. The position-independent correction potential R^{corr} is defined as

$$R^{\text{corr}} = -\Gamma \frac{q}{4\pi a \epsilon_0}.$$

The Abagyan-Totrov modified image approximation to the reaction field is then defined as

$$\Phi_{\text{RF}}(\mathbf{r}) \approx \hat{\Phi}_{\text{AT}}(\mathbf{r}) = R^{(0)}(\mathbf{r}) + R^{\text{corr}}. \quad (34)$$

The reaction field energy based on the Kirkwood image approximation (23), however, reproduces the Born formula when r_s tends to zero. This implies that, when the source is located around the center of the sphere, the Kirkwood image approximation (23) should perform better than the Friedman image approximation (31). On the other hand, one can show that $\hat{\Phi}_{\text{K}}(\mathbf{r}) = \hat{\Phi}_{\text{AT}}(\mathbf{r})$ as r_s tends to zero, indicating that for relatively small values of r_s , the Kirkwood and the Abagyan-Totrov image approximations are comparable in terms of their accuracy. Applications of the Abagyan-Totrov modified image approximation can be found in [1, 32, 17].

3.5 The high-order accurate multiple image approximation

In essence, the image approximations to the reaction field discussed in the previous subsections all employ a single image charge to represent the reaction field with limited accuracy. Recently, a high-order accurate multiple image (MI) approximation to the reaction field was proposed [4, 8, 9] based on (18)-(19). The high-order accurate MI approximation to the reaction field is obtained by representing the continuous line charge $q'(x)$ in (18) with discrete charges constructed through an appropriate numerical quadrature [4]. More precisely, without losing any generality, let $s_m, w_m, m=1, 2, \dots, M$, be the Gauss quadrature points and weights on the interval $[-1, 1]$, which can be obtained with the program ORTHPOL [14]. Then, the numerical quadrature

for approximating the integral in (18) is

$$\int_{r_k}^{\infty} \frac{q'(x)}{4\pi\epsilon_i|\mathbf{r}-\mathbf{x}|} dx \approx \sum_{m=1}^M \frac{q_m}{4\pi\epsilon_i|\mathbf{r}-\mathbf{x}_m|} = \sum_{m=1}^M V[q_m, \mathbf{x}_m, \epsilon_i],$$

where $\mathbf{x}_m=(x_m, 0, 0)$, and for $m=1, 2, \dots, M$,

$$q_m = -\Gamma \frac{\epsilon_i}{2\epsilon_o} \frac{w_m x_m}{a} q, \quad x_m = r_k \left(\frac{2}{1-s_m} \right)^{(\epsilon_i+\epsilon_o)/\epsilon_o}.$$

Accordingly, the high-order accurate multiple image approximation to the reaction field is defined as

$$\begin{aligned} \Phi_{\text{RF}}(\mathbf{r}) &\approx \hat{\Phi}_{\text{MI}}(\mathbf{r}) = \frac{q_{\text{MI}}}{4\pi\epsilon_i|\mathbf{r}-\mathbf{r}_k|} + \sum_{m=1}^M \frac{q_m}{4\pi\epsilon_i|\mathbf{r}-\mathbf{x}_m|} \\ &= V[q_{\text{MI}}, \mathbf{r}_k, \epsilon_i] + \sum_{m=1}^M V[q_m, \mathbf{x}_m, \epsilon_i]. \end{aligned} \quad (35)$$

where $q_{\text{MI}} = \Upsilon q$. Similar multiple image approximation for the potential outside the sphere can be obtained by the same quadrature discretization of (19) [4]. Due to the linear nature of the electrostatic potential from multiple charges, the multiple image approximation (35) to the reaction field can be used for each physical charge individually and then superimposed to produce the total reaction fields of multiple charges.

4 Image Charges for an Aqueous Solvent

In many biological application, we need to consider the ionicity of the solvent for the material outside the sphere. In the Debye-Hückel theory [7], the mobile ion concentration in the ionic solvent is given by a Boltzmann distribution in the mean field approximation. For a solvent of weak ionic strength, the linearized Poisson-Boltzmann equation [12]

$$\nabla^2\Phi(\mathbf{r}) - \lambda^2\Phi(\mathbf{r}) = 0, \quad |r| > a \quad (36)$$

can be used to approximate the screened Coulomb potential in the solvent and Kirkwood expansion can also be found for the solution of (36). Here, λ is the inverse Debye screening length defined by

$$\lambda^2 = \frac{8\pi N_A e^2 \rho_A}{1000\epsilon_o k_B T} c_s, \quad (37)$$

where N_A is Avogadro's number, ρ_A is the solvent density, e is the protonic charge (4.803×10^{-10} esu), k_B is the Boltzmann constant, T is the absolute temperature, and c_s is the ionic concentration measured in molar units. From (37), we see that the inverse Debye screening length λ is proportional to the square root of the ionic concentration c_s . In particular, for 1:1 electrolytes (monovalent:monovalent salts like NaCl), $\lambda \approx 0.33\sqrt{c_s}\text{\AA}^{-1}$ at room temperature (25°), with $\epsilon_o=78.5$ and $\text{\AA}=10^{-10}\text{m}$ [35].

In [8, 9], we have developed various image approximations in the order of the small parameter $u=\lambda a$, for instance, a fourth order approximation is given as follows.

$$\begin{aligned}\Phi_{\text{RF}}(\mathbf{r}) &= \frac{q_K}{4\pi\epsilon_i|\mathbf{r}-\mathbf{r}_K|} + \int_{r_K}^{\infty} \frac{q_{L1}(x)}{4\pi\epsilon_i|\mathbf{r}-\mathbf{x}|} dx + \int_{r_K}^{\infty} \frac{q_{L2}(x)}{4\pi\epsilon_i} \left(\frac{1}{|\mathbf{r}-\mathbf{x}|} - \frac{1}{x} \right) dx \\ &+ \Phi_{C1} + \Phi_{C2}(\mathbf{r}) + \Phi_{C3}(\mathbf{r}) + O(u^4), \quad (38) \\ &= V[q_K, \mathbf{r}_K, \epsilon_i] + \int_{r_K}^{\infty} V[q_{L1}(x), \mathbf{x}, \epsilon_i] dx \\ &+ \int_{r_K}^{\infty} (V[q_{L2}(x), \mathbf{x}, \epsilon_i](\mathbf{r}) - V[q_{L2}(x), \mathbf{x}, \epsilon_i](0)) dx \\ &+ \Phi_{C1} + \Phi_{C2}(\mathbf{r}) + \Phi_{C3}(\mathbf{r}) + O(u^4)\end{aligned}$$

where Φ_{C1} is a *constant, position-independent* correction potential defined as

$$\Phi_{C1} = \frac{q}{4\pi\epsilon_i a} \left(C_0(u) + \Gamma - \frac{\delta_1}{\sigma_1} \right), \quad (39)$$

and on the other hand, $\Phi_{C2}(\mathbf{r})$ is a *position-dependent* correction potential given by

$$\Phi_{C2}(\mathbf{r}) = \frac{q}{4\pi\epsilon_i a} \left(C_1(u) + \Gamma - \frac{\delta_1}{1+\sigma_1} - \frac{\delta_2}{1-\sigma_2} \right) \frac{r}{r_K} \cos\theta. \quad (40)$$

the potential $\Phi_{C3}(\mathbf{r})$ is defined as

$$\Phi_{C3}(\mathbf{r}) = \frac{q}{4\pi\epsilon_i a} \left(C_2(u) + \Gamma - \frac{\delta_1}{2+\sigma_1} - \frac{\delta_2}{2-\sigma_2} \right) \left(\frac{r}{r_K} \right)^2 P_2(\cos\theta). \quad (41)$$

Here, $P_2(\cos\theta) = (3\cos^2\theta - 1)/2$. Also, denoting $\sigma_0 = \frac{\epsilon_o}{\epsilon_i + \epsilon_o}$, $\delta_0 = \frac{\epsilon_i(\epsilon_i - \epsilon_o)}{(\epsilon_i + \epsilon_o)^2}$

$$\begin{aligned}\delta_1 &= \frac{\alpha_2\sigma_1 - \alpha_1}{\sigma_1 + \sigma_2}, & \sigma_1 &= \frac{\sqrt{\beta_2^2 - 4\beta_1} + \beta_2}{2}, \\ \delta_2 &= \frac{\alpha_2\sigma_2 + \alpha_1}{\sigma_1 + \sigma_2}, & \sigma_2 &= \frac{\sqrt{\beta_2^2 - 4\beta_1} - \beta_2}{2}.\end{aligned}$$

$$\alpha_1 = -\Gamma\left(\frac{a_1}{a_3} - \frac{b_1}{b_3}\right), \quad \beta_1 = \frac{b_1}{b_3},$$

$$\alpha_2 = -\Gamma\left(\frac{a_2}{a_3} - \frac{b_2}{b_3}\right), \quad \beta_2 = \frac{b_2}{b_3}.$$

$$a_1 = -(\epsilon_i + \epsilon_o)u^2 - 2(\epsilon_i - \epsilon_o), \quad a_2 = (\epsilon_i - \epsilon_o)(2 - u^2), \quad a_3 = 4(\epsilon_i - \epsilon_o),$$

$$b_1 = -\epsilon_o(2 - u^2), \quad b_2 = -(\epsilon_i + \epsilon_o)u^2 - 2(\epsilon_i - \epsilon_o), \quad b_3 = 4(\epsilon_i + \epsilon_o).$$

And,

$$q_K = -\Gamma \frac{a}{r_S} q,$$

$$q_{L1}(x) = \frac{\delta_1 q}{a} \left(\frac{x}{r_K}\right)^{-\sigma_1}, \quad r_K \leq x. \quad (42)$$

$$q_{L2}(x) = \frac{\delta_2 q}{a} \left(\frac{x}{r_K}\right)^{\sigma_2}, \quad r_K \leq x. \quad (43)$$

Discrete image can be constructed from (38) [9] given as

$$\Phi(\mathbf{r}) \approx \frac{1}{4\pi\epsilon_i} \left(\frac{q_K}{|\mathbf{r} - \mathbf{r}_K|} + \sum_{m=1}^M \frac{q_m^{L1}}{|\mathbf{r} - \mathbf{x}_m|} + \sum_{m=1}^M \frac{q_m^{L2}}{|\mathbf{r} - \mathbf{x}'_m|} \right) + \bar{\Phi}_{C1} + \bar{\Phi}_{C2}(\mathbf{r}) + \bar{\Phi}_{C3}(\mathbf{r}) \quad (44)$$

$$= V[q_K, \mathbf{r}_K, \epsilon_i] + \sum_{m=1}^M V[q_m^{L1}, \mathbf{x}_m, \epsilon_i] + \sum_{m=1}^M V[q_m^{L1}, \mathbf{x}'_m, \epsilon_i] + \bar{\Phi}_{C1} + \bar{\Phi}_{C2}(\mathbf{r}) + \bar{\Phi}_{C3}(\mathbf{r})$$

$$q_m^{L1} = 2^{-\tau\sigma_c} \tau \delta_1 \omega_m \left(\frac{x_m}{r_K}\right)^{\sigma_c - \sigma_1} \frac{x_m}{a} q, \quad (45)$$

and

$$q_m^{L2} = 2^{-\tau\sigma_c} \tau \delta_2 \omega_m \left(\frac{x_m}{r_K}\right)^{\sigma_c + \sigma_2} \frac{x_m}{a} q. \quad (46)$$

Here, $s_m, \omega_m, m=1, 2, \dots, M$, are the Jacobi-Gauss or Jacobi-Gauss-Radau points and weights based on the Jacobi polynomial $P^{(\alpha, \beta)}(x)$ - on the interval $[-1, 1]$ with $\alpha = \tau\sigma - 1$ and $\beta = 0$, with $\tau > 0$. The parameter $\sigma_c > 0$ is tunable for optimal computational efficiency. For example, depending on the value of $u = \lambda a$, either of the two natural choices $\sigma_c = \sigma_1$ and $\sigma_c = 1 - \sigma_2$ could perform better than the other.

5 Conclusions

In this paper, we provide a review of classical image methods for calculating electrostatic potentials for several cases of simple geometries and also recent developments of images for a dielectric sphere with immediate applications in computer simulations of bimolecular and other material systems.

Acknowledgments

The author thanks the support of the National Institutes of Health (grant number: NIGMS 1R01GM083600-01) for the work reported in this paper. Also, the author thanks for the many discussions with Dr. S. Z. Deng, Donald Jacobs, and Andriy Baumketner during the writing of this paper.

References

- [1] R. Abagyan and M. Totrov, Biased probability Monte Carlo conformational searches and electrostatic calculations for peptides and proteins, *J. Mol. Biol.* 235 (1994) 983-1002.
- [2] N.A. Baker, Improving implicit solvent simulations: a Poisson-centric view, *Curr. Opin. Struct. Biol.* 15 (2005) 137-143.
- [3] M. Born, *Z. Phys.* 1 (1920) 45.
- [4] W. Cai, S. Deng and D. Jacobs, Extending the fast multipole method to charges inside or outside a dielectric sphere, *J. Comput. Phys.* 223 (2007) 846-864.
- [5] H. Cheng, On the method of images for systems of closely spaced conducting spheres, *SIAM J. Appl. Math.* 61 (2000) 1324-1337.
- [6] H. Cheng and L. Greengard, A method of images for the evaluation of electrostatic fields in system of closely spaced conducting cylinders, *SIAM J. Appl. Math.* 58 (1998) 122-141.
- [7] P. Debye and E. Hückel, The theory of electrolytes. I. Lowering of freezing point and related phenomena, *Physikalische Zeitschrift* 24 (1923) 185-206.
- [8] S. Deng and W. Cai, Discrete image approximations of ionic solvent induced reaction field to charges, *Communications in Computational Physics* 2 (2007) 1007-1026.

- [9] S. Deng and W. Cai, Extending the fast multipole method for charges inside a dielectric sphere in an ionic solvent: high order image approximations for reaction fields, to appear in *J. Comput. Phys.*, 2008.
- [10] M. Feig and C.L. Brooks III, Recent advances in the development and application of implicit solvent models in biomolecule simulations, *Curr. Opin. Struct. Biol.* 14 (2004) 217-224.
- [11] A.V. Finkelstein, Electrostatic interactions of charged groups in an aqueous medium and their effect on the formation of polypeptide chain secondary structure, *Molecular Biology*, 1977, 627-634.
- [12] F. Fogolari, A. Brigo and H. Molinari, The Poisson-Boltzmann equation for biomolecular electrostatics: a tool for structural biology. *J Mol Recognit* 15 (2002) 377-92.
- [13] H.L. Friedman, Image approximation to the reaction field, *Mol. Phys.* 29 (1975) 1533-1543.
- [14] W. Gautschi, Algorithm 726; ORTHPOL - a package of routines for generating orthogonal polynomials and Gauss-type quadrature rules, *ACM Trans. Math. Softw.* 20 (1994) 21-62.
- [15] L. Greengard, *The Rapid Evaluation of Potential Fields in Particle Systems*, MIT, Cambridge, 1987.
- [16] L. Greengard and V. Rokhlin, A fast algorithm for particle simulations, *J. Comput. Phys.* 73 (1987) 325-348.
- [17] J.J. Havranek and P.B. Harbury, Tanford-Kirkwood electrostatics for protein modeling, *Proc. Natl. Acad. Sci. USA* 96 (1999) 11145-11150.
- [18] E. Honein, T. Honein and G. Herrmann, On two circular inclusions in harmonic problems, *Quart. Appl. Math.* 50 (1992) 479-499.
- [19] J.G. Kirkwood, Theory of solutions of molecules containing widely separated charges with special applications to awitterions, *J. Chem. Phys.* 2 (1934) 351-361.
- [20] J.G. Kirkwood, Statistical mechanics of liquid solutions, *Chem. Rev.* 19 (1936) 275-307.
- [21] P. Koehl, Electrostatics calculations: latest methodological advances, *Curr. Opin. Struct. Biol.* 16 (2006) 142-151.

- [22] M.S. Lee and M.A. Olson, Evaluation of Poisson solvation models using a hybrid explicit/implicit solvent method, *J. Phys. Chem. B* 109 (2005) 5223-5236.
- [23] M.S. Lee, F.R. Salsbury Jr. and M.A. Olson, An efficient hybrid explicit/implicit solvent method for biomolecular simulations, *J. Comput. Chem.* 25 (2004) 1967-1978.
- [24] R.M. Levy and E. Gallicchio, Computer simulations with explicit solvent: recent progress in the thermodynamic decomposition of free energies and in modeling electrostatic effects, *Annu. Rev. Phys. Chem.* 49 (1998) 531-567.
- [25] I.V. Lindell, Electrostatic image theory for the dielectric sphere, *Radio Sci.* 27 (1992) 1-8.
- [26] J.C. Maxwell, *A treatise on electricity and magnetism*, 1 (1891), 3rd ed., reprint, Dover, New York, 1954.
- [27] P.M. Morse and H. Feshbach, *Methods of Theoretical Physics*, McGraw-Hill, New York, 1953.
- [28] C. Neumann, *Hydrodynamische Untersuchungen nebst einem Anhang über die Probleme der Electrostatik und der magnetischen Induktion*, Teubner, Leipzig, 1883, 279-282.
- [29] K.I. Nikoskinen and I.V. Lindell, Image solution for Poisson's equations in wedge geometry, *IEEE trans. Ant. & Prop.* 43 (1995) 179-187.
- [30] W.T. Norris, Charge images in a dielectric sphere, *IEE Proc.-Sci. Meas. Technol.* 142 (1995) 142-150.
- [31] A. Okur and C. Simmerling, Hybrid explicit/implicit solvation methods, in: D. Spellmeyer (Ed.), *Annu. Rep. Comput. Chem.*, Vol. 2, 2006, Chapter 6.
- [32] G. Petraglio, Nonperiodic boundary conditions for solvated systems, *J. Chem. Phys.* 123 (2005) 044103.
- [33] J.A.C. Rullmann and P.Th.V. Duijnen, Analysis of discrete and continuum dielectric models: application to the calculation of protonation energies in solution, *Mol. Phys.* 61 (1987) 293-311.
- [34] C. Sagui and T.A. Darden, Molecular dynamics simulation of biomolecules: long-range electrostatic effects, *Annu. Rev. Biophys. Biomol. Struct.* 28 (1999) 155-179.

- [35] T. Schlick, *Molecular Modeling and Simulation: An Interdisciplinary Guide*, Springer, New York, 2002.
- [36] W.E. Smith and J. Rungis, Twin adhering conducting spheres in an electric field - an alternative geometry for an electrostatic voltmeter, *J. Phys. E.* 8 (1975) 379-382.
- [37] W. Smythe, *Static and Dynamic Electricity*, Taylor & Francis; 1 edition (January 1, 1989).
- [38] J.C.-E. Sten and K.I. Nikoskinen, Image polarization and dipole moment of a cluster of two similar conducting spheres, *J. Electrostatics* 35 (1995) 267-277.
- [39] A. Wallqvist, On the implementation of Friedman boundary conditions in liquid water simulations, *Mol. Simul.* 10 (1993) 13-17.
- [40] L. Wang and J. Hermans, Reaction field molecular dynamics simulation with Friedman's image method, *J. Phys. Chem.* 99 (1995) 12001-12007.