Fast Algorithms for Electrostatic Interactions in Molecular Simulations with Image Methods for Reaction Fields

Wei Cai
University of North Carolina at Charlotte

Summary: We have developed a new multiple image charge formula for accurate calculation of the reaction field within a spherical cavity embedded in a continuum. The implementation of this formula will improve the speed and accuracy of current electrostatic interaction algorithms for molecular simulations with applications in protein folding and material damages under irradiation.

Coulomb interactions of electrostatic charges play critical role in understanding phenomena of many complex inhomogeneous systems such as the irradiation damages of materials and the solvation free energy of biomolecules in ionic solvent.

For example, in a reaction field model of salvation of biomolecules, the electrostatic interactions are treated both explicitly and implicitly. Considering a local volume V_{in} of spherical shape embedded in a solvent, molecules inside this cavity will have Coulomb interactions between all pairs of charges - assuming a dielectric constant of ε_i, which is often set to be the permittivity of free space or slightly greater. Outside this cavity, the effect of bulk solvent is represented by a continuum medium with dielectric ε_o. The electrostatic problem is formulated with a Poisson equation for charge distribution inside V_{in} contains all explicit charges ρ_{in} from the solute and solvent molecules. On the interface, the continuity of the tangential component of the electric field and the normal component of the displacement field will be enforced.

The solution Φ of the Poisson equation inside the cavity V_{in} can be written in terms of the primary field from the charge distribution and the Reaction Field (RF) for ρ_{in} due to the polarization of the solvent in V_{out}, namely, we have $\Phi = \Phi_\rho + \Phi^{RF}$.

Friedman in 1975 [1] proposed an image method for Φ^{RF} in the case of a dielectric sphere , which is accurate only to the order of $\varepsilon_{\text{i}} / \varepsilon_{\text{o}}$, typically resulting in more than 1% error, and has been used regularly in molecular dynamic simulations. Despite of further efforts, not much improvement on the image method has been made since Friedman's work·

In contrast, the advantage of our new reaction field method for a spherical cavity is to use an *exact analytical result for Poisson equation in terms of discrete image charges.*

$$\Phi^{RF}(r) \approx \frac{q_{kevin}}{4\pi\varepsilon_i \,|\, r - r_{kevin} \,|} + \sum_{m=1}^{M} \frac{q'_m}{4\pi\varepsilon_i \,|\, r - x_m \,|},$$

where $r_{\text{kelvin}} = a^2 / r_{\text{s}}$ is the Kelvin image location and $q_{\text{kelvin}} = \gamma a q / r_{\text{s}}$ the Kevin image magnitude, and the magnitude and the location of remaining discrete image charges are defined explicitly as

*704-687-4581, wcai@uncc.edu

$$q'_m = 2^{\frac{\gamma-1}{2}\tau-1}\gamma(1+\gamma)\tau\omega_m q\frac{x_m}{a} \ ,$$

$$x_m = r_{\text{kelvin}}\left(\frac{2}{1-s_m}\right)^{\tau} \ ,$$

where $\gamma = \dfrac{\varepsilon_{in}-\varepsilon_o}{\varepsilon_{in}+\varepsilon_o}$, $\tau = 2/(1-\gamma)$ and $\{\omega_m, s_m\}_{m=1}^{M}$ are Gauss quadrature weights and points based on the M-th order Jacobi polynomial. The convergence of this image approximation can be achieved by increasing the polynomial order M.

The number of image charges required to yield a desired relative error in the reaction field depends on the source location. Table 1 shows the level of accuracy that can be achieved. For example, with 3 or less discrete image charges, a 10^{-3} relative error in the reaction field can be obtained for source charges positioned anywhere within 0.9 of the sphere radius.

Table 1: Number of image charges to yield a desired relative error in the RF for a specified source location as a fraction of the sphere radius. (r_s – source charge location, a - sphere radius).

$\frac{r_s}{a}$	.01	.1	.3	.5	.7	.9	0.95	0.99
10^{-2}	2	2	2	2	2	2	2	2
10^{-3}	2	2	2	2	3	3	4	5
10^{-4}	2	2	3	3	4	5	7	10
10^{-5}	2	2	3	4	5	8	10	17

These image charges are well suited for the Fast Multipole Method (FMM). Consequently: *The powerful FMM previously available for homogeneous systems can now be extended to non-homogeneous systems.* An $O(N)$ complexity has been achieved in the calculation of electrostatic potential of N charges inside or outside a dielectric sphere with the combination of the FMM and the method of images [2]. Therefore, unlike all other methods, the reaction field can be calculated accurately and efficiently throughout the cavity in one calculation, without periodic boundary condition. .

In conclusion, for many scientific and engineering applications involving biopolymers, such as proteins, the multiple image approach presented here will provide a new fast numerical solver to the Poisson equation. Based on this image charge result, we can successfully extend the FMM [2] to calculate electrostatic interactions for charges inside or outside a dielectric sphere. The generality and simplicity of the presented formula should produce a far-reaching impact on computational simulations for chemical and biological systems involving electrostatic interactions within a solvent.

References:

[1] H. L. Friedman, "Image approximation to the reaction field," Mol. Phys. 29, 1533-1543 (1975).

[2] W. Cai, S. Z. Deng, D. Jacobs, Extending the Fast Multipole Method to Charges Inside or Outside a Dielectric Sphere, *the Journal of Computational Physics*, Vol. 223, Issue 2, 1 May 2007, Pages 846-864

For further information on this subject contact:

Dr. Wei Cai
Dept of Mathematics, UNC Charlotte
wcai@uncc.edu
704-687-4581

Or

Dr. Anil Deane
Applied Mathematics Research Program
Office of Advanced Scientific Computing
Phone: 301-903-1465
deane@ascr.doe.gov