A simple non-Ewald scheme for calculating electrostatic interactions of charged particle systems: the zero-dipole summation method and the application to molecular systems

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Appropriate treatment of the electrostatic interaction of N particles with point charges $\{q_1,\ldots,q_N\}$ and positions $(\mathbf{r}_1,...,\mathbf{r}_N)$, represented as the Coulombic energy, $\frac{1}{2}\sum_{i=1}^{N}\sum_{j} q_i q_j / \| \mathbf{r}_i - \mathbf{r}_j \|$, is critical for computational study of materials in a realistic manner. Here, the manner of the summation with respect to j depends on the boundary conditions.

Until recently, the periodic boundary condition (PBC) has been used in many of these simulations with the aid of lattice sum (LS) methods, such as the Ewald method or its variants. Such protocols are quite natural for applying to an inherently periodic system, and they are useful to treat an isotropic bulk system because the PBC enables us to avoid the creation of an interface. In contrast, for an intrinsically non-periodic system, the interactions from the infinite copies imposed from the PBC are clearly unphysical. From a computational viewpoint, a mesh-based approach for accelerating the LS scheme is commonly used, where the fast Fourier transform is employed for discrete Fourier transforms. However, the Fourier part requires all to all communications in a parallel computation, which lead to a heavy task for a large system. In addition, such a mesh-based approach often includes other side effects, such as the violation of Newton's law—conservation of the total momentum. These side effects come from the fact that the devised charge distribution expanded on the mesh is not necessarily compatible with the total-force vanishing (translational invariance of the potential function), which should hold, e.g., if the system is governed by the law of action and reaction.

In contrast, cutoff-based (CB) approaches for estimating the electrostatic interaction can be applied to any boundary conditions in principle. They are simple, computationally very demanded, and conserving the total momentum of the system, as long as a pairwise summation of a certain smooth potential function is utilized under a suitable truncation protocol. In addition, a positive motivation for employing the CB methods are provided, if we consider that the actual interactions in condensed matters are essentially screened, compared with the bare Coulombic form, due to sufficient electric cancellations via a suitable assembling of positive or negative charges. Thus, the problem of the CB methods is to improve the accuracy to an acceptable level and eliminate their artifacts, which have often been pointed out, with maintaining their advantages.

We introduced a novel idea, zero-dipole summation, which is based on the CB approach. This summation prevents the nonzero-charge and nonzero-dipole states artificially generated by a simple cutoff truncation, which often causes large energetic noises and several significant artifacts [1]. In the presentation, we first discuss the theoretical details, including the assumption and derivation, of our method. We will discuss the computational timing of the method to show that the simple pairwise form enables us to actually conduct high-performance parallel computation. We will also exhibit the numerical results of molecular dynamics simulations by applying our method. The accuracies, stabilities, and static and dielectric properties of molecular systems were investigated. We obtained very accurate results, including for the electrostatic energy and the distance-dependent Kirkwood factor for a water system [2]. In particular, the latter quantity is highly sensitive to the treatment of the electrostatic interaction, leading to failures for many CB methods. Accurate descriptions were obtained in a membrane protein system, composed from explicit ions and membrane and water molecules, and also in a DNA system. Finally, we would like to discuss the relationships and differences between the current method and the other promising CB methods [3], such as the Wolf method [4] and the pre-averaging method [5].

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