

Point Multipoles in the Ewald Summation (Revisited)

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This article describes how to incorporate point charges, dipoles and quadrupoles (or combinations of them i.e. point multipoles) into the Ewald summation method. A full description of the multipole potential, forces and torques in a periodic system is provided.

1 Introduction

This article is a re-draft of a much earlier paper, which appeared in the CCP5 Newsletter as long ago as 1982! [1]. The article is now effectively out of print and, more to the point, is not accessible over the Web. However, it is apparent that the subject matter is still of interest (long range forces being an eternal problem in modelling molecular systems!), and since I still receive requests for reprints, I have therefore reproduced this draft for electronic circulation. The basic description follows that of the earlier paper, but I have added a few more points of explanation and tried to clean up the notation a little.

The purpose of this article is to outline a low level treatment of point multipoles in an Ewald summation[2]. A point multipole in this application is defined as the superposition of a point charge, point dipole and point quadrupole, with no higher terms. Such a multipole might be obtained from an arbitrary charge distribution resolved into these components. The method is capable of extension to higher order, but since it is based on a Cartesian representation, it rapidly becomes too cumbersome to be completely general. However for many systems higher orders of multipole are not necessary and the method is then worth considering. The physical properties described in this article are the potential, force and torque experienced by a point multipole in an infinite periodic system of unit cells containing irregularly spaced multipoles.

The following section describes a number of mathematical operators which are used to define the multipole and derive the multipolar Ewald summation. Section 3 derives the Ewald expression for the potential of a multipole in a periodic system. Section 4 derives the force on the multipole and Section 5 the torque, both of which are essential for molecular dynamics simulation. Some practical comments on the application of the method follow in Section 6, with conclusions in Section 7.

2 Multipole Operators

Taylor's expansion for a scalar function of three variables (i.e. $F(x, y, z)$ or $F(\underline{r})$) may be written as:

$$F(\underline{r} + \delta\underline{r}) = F(\underline{r}) + \sum_{\alpha} \delta r^{\alpha} \frac{\partial}{\partial r^{\alpha}} F(\underline{r}) + \frac{1}{2} \sum_{\alpha} \sum_{\beta} \delta r^{\alpha} \delta r^{\beta} \frac{\partial^2}{\partial r^{\alpha} \partial r^{\beta}} F(\underline{r}) + \dots etc, \quad (1)$$

with $\alpha, \beta = x, y, z$ etc. It is convenient to write this expansion in the following form.

$$F(\underline{r} + \delta\underline{r}) = F(\underline{r}) + \delta\underline{r} \cdot \hat{\nabla} F(\underline{r}) + \underline{U} : \hat{\underline{\Omega}} + \dots etc. \quad (2)$$

where \underline{U} is a (3×3) matrix with components

$$U^{\alpha\beta} = \frac{1}{2} \delta r^{\alpha} \delta r^{\beta} \quad etc. \quad (3)$$

$\hat{\nabla}$ is the familiar vector operator

$$\hat{\nabla} = i \frac{\partial}{\partial x} + j \frac{\partial}{\partial y} + k \frac{\partial}{\partial z}, \quad (4)$$

while $\hat{\underline{\Omega}}$ a matrix operator of dimension (3×3) defined by its components:

$$\hat{\Omega}^{\alpha\beta} = \frac{\partial^2}{\partial r^{\alpha} \partial r^{\beta}} \quad etc. \quad (5)$$

The operation indicated by the colon ($:$) is the dyadic scalar product of two matrices i.e.

$$\underline{A} : \underline{B} = \sum_{\alpha} \sum_{\beta} A^{\alpha\beta} B^{\alpha\beta}. \quad (6)$$

The equivalence of the forms (1) and (2) follows easily from these definitions. (The terms of the series (2) are therefore to be regarded as consecutive contractions of tensors of rank 0,1,2, ... etc. to yield a scalar result.)

Consider a cluster of n point charges (q_k) scattered about the origin at respective positions \underline{r}_k and a *unit* point charge at a *large* distance \underline{r} from the origin. The electrostatic potential of the unit point charge is then given by

$$V(\underline{r}) = \frac{1}{4\pi\epsilon_o} \sum_{k=1}^n \frac{q_k}{|\underline{r} - \underline{r}_k|}. \quad (7)$$

Seen from the location \underline{r} , the charge cluster may be regarded as a multipole located at the origin, since the vectors \underline{r}_k are assumed small in comparison with the distance \underline{r} (i.e. $r \gg r_k$). Thus the expansion (2) may be used with (7) to obtain the following expression for $V(\underline{r})$ (in which contributions above quadrupole are ignored.)

$$V(\underline{r}) = \frac{1}{4\pi\epsilon_o} \left\{ C_a - \underline{D}_a \cdot \hat{\nabla} + \underline{Q}_a : \hat{\underline{\Omega}} \right\} \left\{ \frac{1}{r} \right\}, \quad (8)$$

where

$$C_a = \sum_{k=1}^n q_k \quad (9)$$

is the net multipole charge,

$$\underline{D}_a = \sum_{k=1}^n q_k \underline{r}_k \quad (10)$$

is the net multipole dipole, and

$$\underline{\underline{Q}}_a = \sum_{k=1}^n q_k \underline{\underline{U}}_k \quad (11)$$

is the net multipole quadrupole. In these formulae, the suffix a is to be regarded as an index of the whole cluster i.e. the multipole M_a . The multipole is to be regarded as a rigid entity (i.e. the charges q_k have a fixed displacement relative to each other.)

From (8) a multipole operator \hat{M}_a may be defined:

$$\hat{M}_a = C_a - \underline{D}_a \cdot \hat{\nabla} + \underline{\underline{Q}}_a : \hat{\underline{\underline{\Omega}}}, \quad (12)$$

with the aid of which (8) becomes

$$V(\underline{r}) = \frac{1}{4\pi\epsilon_o} \hat{M}_a \left\{ \frac{1}{r} \right\}. \quad (13)$$

It is therefore apparent that the potential at \underline{r} , due to a point multipole at the origin, is obtained by applying the operator \hat{M}_a to the expression describing the potential due to a unit positive charge at the origin.

By a similar reasoning it may be deduced that the potential $\Phi(\underline{r})$ of a second point multipole (M_b) positioned at \underline{r} , due to the potential field $V(\underline{r})$ of the first, is given by

$$\Phi(\underline{r}) = \hat{M}_b V(\underline{r}) \quad (14)$$

or

$$\Phi(\underline{r}) = \frac{1}{4\pi\epsilon_o} \hat{M}_b \hat{M}_a \left\{ \frac{1}{r} \right\}, \quad (15)$$

where

$$\hat{M}_b = C_b + \underline{D}_b \cdot \hat{\nabla} + \underline{\underline{Q}}_b : \hat{\underline{\underline{\Omega}}} \quad (16)$$

The force acting on the second multipole will be given by applying the usual operator $-\hat{\nabla}$ to the expression (15)

$$\underline{F}_b = -\frac{1}{4\pi\epsilon_o} \hat{\nabla} \hat{M}_b \hat{M}_a \left\{ \frac{1}{r} \right\}. \quad (17)$$

The torque acting on the second multipole in the potential field of the first may be written as

$$\underline{T}_b = - \sum_{k=1}^n q_k \underline{r}_k \times \hat{\underline{V}} V(\underline{r} + \underline{r}_k) \quad (18)$$

from which it may be deduced that

$$\underline{T}_b = -\{\underline{D}_b \times \hat{\underline{V}} + 2\underline{Q}_b \times \hat{\underline{\Omega}}\}V(\underline{r}), \quad (19)$$

leading to the following definition of the torque operator:

$$\hat{T}_b = -\{\underline{D}_b \times \hat{\underline{V}} + 2\underline{Q}_b \times \hat{\underline{\Omega}}\}. \quad (20)$$

The operation implied by \times is a vector product. The vector product of two vectors is well known, the vector product of two matrices however needs explaining. It is defined as the resultant vector \underline{V} of two matrices \underline{A} and \underline{B} according to the formula

$$V^\alpha = \sum_{\beta} \{A^{\alpha+1,\beta} B^{\alpha+2,\beta} - A^{\alpha+2,\beta} B^{\alpha+1,\beta}\}, \quad (21)$$

where indices exceeding the matrix dimension (3 in this case) are regarded as cyclic permutations. It is apparent that the vector product of two matrices is non-commutative, with

$$\underline{A} \times \underline{B} = -\underline{B} \times \underline{A} \quad (22)$$

These operators are sufficient to derive the required expressions in the Ewald summation.

3 The Ewald Summation

The electrostatic potential at a point \underline{r} (*not* a multipole site) in an infinite periodic system of unit point charges (which may be randomly distributed throughout the unit cell¹) is given by the Ewald summation [2] as:

$$\begin{aligned} V_E(\underline{r}) = & \frac{1}{V_o \epsilon_o} \sum_{\underline{k} \neq \underline{0}}^{\infty} A(k) \sum_j^N \exp(-i\underline{k} \cdot (\underline{r}_j - \underline{r})) \\ & + \frac{1}{4\pi \epsilon_o} \sum_j^{\infty} B_0(|\underline{r}_j - \underline{r}|) \end{aligned} \quad (23)$$

where

$$A(k) = \left\{ \frac{1}{k^2} \right\} \exp(-k^2/4\xi^2) \quad (24)$$

¹The unit cell in this context is, of course, the simulation cell

$$B_0(u) = \left\{ \frac{1}{u} \right\} \operatorname{erfc}(\xi u), \quad (25)$$

$$\operatorname{erfc}(\xi u) = \frac{2}{\sqrt{\pi}} \int_{\xi u}^{\infty} \exp(-s^2) ds, \quad (26)$$

and N is the number of point charges in the unit (simulation) cell, ξ is Ewald's convergence parameter, V_o is the volume of the unit cell. \underline{k} is a reciprocal lattice vector obtained from the unit cell width (L) for a cubic system:

$$\underline{k} = \frac{2\pi}{L} (n_a, n_b, n_c)^\dagger, \quad (27)$$

where n_a, n_b and n_c are integers.

According to the principles outlined in the previous section Ewald's summation may be adapted to a system of point multipoles by applying the set of operators \hat{M}_j defined by

$$\hat{M}_j = C_j - \underline{D}_j \cdot \hat{\nabla} + \underline{Q}_j : \hat{\underline{\Omega}}, \quad (28)$$

Following this prescription we obtain the following expression, which describes the potential of a unit positive charge inserted into a system of point multipoles:

$$\begin{aligned} V(\underline{r}) = & \frac{1}{V_o \epsilon_o} \sum_{\substack{\infty \\ \underline{k} \neq 0}} A(k) \sum_j^N (C_j - i \underline{D}_j \cdot \underline{k} - \underline{Q}_j : \underline{K}) \exp(-i \underline{k} \cdot (\underline{r}_j - \underline{r})) + \\ & \frac{1}{4\pi \epsilon_o} \sum_j^\infty (C_j B_0(|\underline{r}_j - \underline{r}|) - (\underline{D}_j \cdot (\underline{r}_j - \underline{r}) + \underline{Q}_j : \underline{I}) B_1(|\underline{r}_j - \underline{r}|) + \\ & \underline{Q}_j : \underline{R}_j B_2(|\underline{r}_j - \underline{r}|)) \end{aligned} \quad (29)$$

where \underline{K} and \underline{R}_j are matrices defined as follows:

$$\underline{K}^{\alpha\beta} = k^\alpha k^\beta \quad (etc.) \quad (30)$$

$$\underline{R}_{jg}^{\alpha\beta} = r_{jg}^\alpha r_{jg}^\beta \quad (etc.) \quad (31)$$

$$(32)$$

The functions $B_\ell(|\underline{r}_j - \underline{r}|)$ are derived from $B_0(|\underline{r}_j - \underline{r}|)$ according to the recurrence relation

$$B_\ell(u) = \frac{1}{u^2} \left\{ (2\ell - 1) B_{\ell-1}(u) + \frac{(2\xi^2)^\ell}{\xi \sqrt{\pi}} \exp(-\xi^2 u^2) \right\}. \quad (33)$$

Further properties of these important functions are given in the appendix.

To find the potential energy of an interstitial or 'guest' multipole inserted at the position \underline{r} within the system, (but not at an existing multipole site,) a second operator \hat{M}_g must be applied (*c.f.* equation 14), where

$$\hat{M}_g = C_g + \underline{D}_g \cdot \hat{\nabla} + \underline{Q}_g : \hat{\underline{\Omega}}. \quad (34)$$

The result of this operation is

$$\begin{aligned} \phi_g = & \frac{1}{V_o \epsilon_o} \sum_{\underline{k} \neq \underline{0}}^{\infty} A(k) \sum_j^N F_{jg}(\underline{k}) \exp(-i\underline{k} \cdot \underline{r}_{jg}) + \\ & \frac{1}{4\pi \epsilon_o} \sum_{\ell}^4 \sum_j^{\infty} G_{jg}^{\ell}(r_{jg}) B_{\ell}(r_{jg}). \end{aligned} \quad (35)$$

The functions $A(k)$ and B_{ℓ} have already been described. Vector \underline{r}_g is the position adopted by the guest multipole and

$$\underline{r}_{jg} = \underline{r}_j - \underline{r}_g \quad (36)$$

is the separation vector, for which r_{jg} is the scalar separation. The *scalar* functions $F_{jg}(\underline{k})$ and $G_{jg}^{\ell}(\underline{r}_{jg})$ are as follows:

$$F_{jg}(\underline{k}) = (C_g + i\underline{D}_g \cdot \underline{k} - \underline{Q}_g : \underline{K} : \underline{K})(C_j - i\underline{D}_j \cdot \underline{k} - \underline{Q}_j : \underline{K} : \underline{K}) \quad (37)$$

$$G_{jg}^0(\underline{r}_{jg}) = C_g C_j \quad (38)$$

$$G_{jg}^1(\underline{r}_{jg}) = \underline{D}_g \cdot \underline{D}_j + C_j(\underline{D}_g \cdot \underline{r}_{jg} - \underline{Q}_g : \underline{I} : \underline{I}) - C_g(\underline{D}_j \cdot \underline{r}_{jg} + \underline{Q}_j : \underline{I} : \underline{I}) \quad (39)$$

$$\begin{aligned} G_{jg}^2(\underline{r}_{jg}) = & C_j \underline{Q}_g : \underline{R}_{jg} + C_g \underline{Q}_j : \underline{R}_{jg} - 2\underline{Q}_g : \underline{\Delta}_{jg} - 2\underline{Q}_j : \underline{\Delta}_{gj} + \\ & \underline{D}_j \cdot \underline{r}_{jg} \underline{Q}_g : \underline{I} - \underline{D}_g \cdot \underline{r}_{jg} \underline{Q}_j : \underline{I} - \underline{D}_g \cdot \underline{r}_{jg} \underline{D}_j \cdot \underline{r}_{jg} \\ & + 2\underline{Q}_g : \underline{Q}_j + \underline{Q}_g : \underline{I} \underline{Q}_j : \underline{I} \end{aligned} \quad (40)$$

$$\begin{aligned} G_{jg}^3(\underline{r}_{jg}) = & \underline{D}_g \cdot \underline{r}_{jg} \underline{Q}_j : \underline{R}_{jg} - \underline{D}_j \cdot \underline{r}_{jg} \underline{Q}_g : \underline{R}_{jg} - \\ & \underline{Q}_g : \underline{I} \underline{Q}_j : \underline{R}_{jg} - \underline{Q}_j : \underline{I} \underline{Q}_g : \underline{R}_{jg} - 4\underline{Q}_g : \underline{\Theta}_{jg} \end{aligned} \quad (41)$$

$$G_{jg}^4(\underline{r}_{jg}) = \underline{Q}_g : \underline{R}_{jg} \underline{Q}_j : \underline{R}_{jg} \quad (42)$$

where

$$\underline{\Delta}_{ij}^{\alpha\beta} = D_i^{\alpha} r_{ji}^{\beta} \quad (etc.) \quad (43)$$

$$\underline{\Theta}_{ji}^{\alpha\beta} = r_{ji}^{\alpha} \sum_{\gamma} Q_j^{\beta\gamma} r_{ji}^{\gamma} \quad (44)$$

(It is important to note that the interchange of multipole indices i and j in these formulae does not imply taking the transpose, but instead identifies a physically distinct matrix.)

Usually however it is not the potential of a guest multipole that is required, but of one of the multipoles of the system itself. Physically this means equivalencing the guest multipole to one of the multipoles of the system. The above formulae can be adapted to this circumstance in the following way.

1. The terms involving *both* the guest multipole (index g) and the multipole of interest (index i) must be extracted from equation (35). These terms are dealt with below.
2. In the remaining terms involving the guest multipole, the index g is changed to i . Thus as far as these terms are concerned, the guest multipole and the multipole with index i are one and the same.

Now examining the terms separated out from (35) according to (a), it is clear that if the guest multipole is to be equivalenced to the i 'th multipole, these terms represent a 'self interaction' energy in which the separation r_{ig} is zero. These terms are mathematically indeterminate and unphysical but it is not correct simply to neglect them, as the following treatment shows.

Extracting firstly the G_{ig}^ℓ terms from the right of (35) gives

$$\phi^s = \frac{1}{4\pi\epsilon_o} \sum_{\ell}^4 G_{ig}^\ell(\underline{r}_{ig}) B_{\ell}(r_{ig}). \quad (45)$$

Where ϕ^s is used to represent the extracted self interaction terms. Putting \underline{u} to represent the vector \underline{r}_{ig} , it becomes clear from the definition of the functions $B_{\ell}(u)$ in equations (25) and (33) that this expression becomes indeterminate when \underline{r}_g and \underline{r}_i are equivalenced (i.e. as $u \rightarrow 0$). However, expanding the $B_{\ell}(u)$ functions as polynomials in the argument u (see appendix) allows ϕ^s to be rewritten as

$$\phi^s = \frac{1}{4\pi\epsilon_o} \sum_{\ell}^4 G_{ig}^\ell(\underline{u}) \left\{ \frac{(2\ell)!}{\ell! 2^{\ell} u^{2\ell+1}} - \frac{(2\xi^2)^{\ell+1}}{(2\ell+1)\xi\sqrt{\pi}} + O_{\ell}(u) \right\}, \quad (46)$$

where $O_{\ell}(u)$ represents a sum of terms in u and higher powers of u . It is now clear that it is the first terms within the brackets on the right of this expansion that become indeterminate as u tends to zero. However on further inspection it is also clear that these terms are nothing more than the conventional (or non-Ewald) terms defining the potential energy function of two multipoles separated by the distance u . Given this identification, these terms can simply be removed, since they represent an interaction that does not physically exist. It is also apparent that the $O_{\ell}(u)$ terms will vanish as u tends to zero, leaving the only surviving terms as

$$\phi^s = -\frac{1}{4\pi\epsilon_o} \sum_{\ell}^4 \left\{ \frac{(2\xi^2)^{\ell+1} G_{ii}^{\ell}(\underline{0})}{(2\ell+1)\xi\sqrt{\pi}} \right\}. \quad (47)$$

That these terms survive is of course due to the fact that the Ewald method replaces the point multipoles by a superposition of both 'Gaussian' multipoles and the original point multipoles. Removing the point multipole terms leaves the Gaussian contributions intact.

Two further comments are in order. Firstly, the identification of the first terms of (46) with the interaction potential of two multipoles, means that the expression (47) represents a *complete* correction for the self interaction term. It follows that no further correction need be made to the

Fourier component of (35), other than the substitution of index i for g . Secondly, from the identities (38) to (42) it can be seen that the $G_{ii}^\ell(\underline{0})$ terms have no distance dependent contributions, leading to the final form for the self interaction term ϕ_i^s :

$$\phi_i^s = -\frac{2\xi}{4\epsilon_o\sqrt{\pi^3}} \left\{ C_i^2 + 2\xi^2 \left[\frac{1}{3}(D_i^2 + 2C_i\underline{Q}_i : \underline{I}) + \frac{2\xi^2}{5}(2\underline{Q}_i : \underline{Q}_i + (\underline{Q}_i : \underline{I})^2) \right] \right\}, \quad (48)$$

where the index i has been added to ϕ_i^s to express its dependence on the i 'th multipole. The final equation for the potential energy of a multipole in a periodic system of point multipoles is therefore

$$\begin{aligned} \phi_i &= \frac{1}{V_o\epsilon_o} \sum_{\underline{k} \neq \underline{0}}^{\infty} A(k) \sum_j^N F_{ji}(\underline{k}) \exp(-i\underline{k} \cdot \underline{r}_{ji}) + \\ &\quad \frac{1}{4\pi\epsilon_o} \sum_{\ell}^4 \sum_{j \neq i}^{\infty} G_{ji}^\ell(\underline{r}_{ji}) B_\ell(r_{ji}) + \phi_i^s. \end{aligned} \quad (49)$$

From this it is easy to obtain the total configuration energy (per simulation cell) for the system, which is

$$\begin{aligned} U_c &= \frac{1}{2V_o\epsilon_o} \sum_{\underline{k} \neq \underline{0}}^{\infty} A(k) \left| \sum_j^N f_j(\underline{k}) \exp(-i\underline{k} \cdot \underline{r}_j) \right|^2 + \\ &\quad \frac{1}{4\pi\epsilon_o} \sum_{\ell}^4 \sum_i^N \sum_{j>i}^{\infty} G_{ji}^\ell(\underline{r}_{ji}) B_\ell(r_{ji}) + \frac{1}{2} \sum_i^N \phi_i^s. \end{aligned} \quad (50)$$

where

$$f_j(\underline{k}) = C_j - i\underline{D}_j \cdot \underline{k} - \underline{Q}_j : \underline{K}. \quad (51)$$

It is easy to show that this formula reduces to the standard Ewald summation for point charges [2] if the dipoles and quadrupoles are set to zero. It may also be shown that setting the charges and quadrupoles to zero provides the familiar Kornfeld expression for a lattice of point dipoles [2, 3].

4 The Force on a Multipole

According to the prescription in equation (17), the force acting of the i 'th multipole in a lattice of multipoles is obtained by applying the operator $-\hat{\nabla}_i$ to the potential function in equation (49). The result is

$$\begin{aligned} \underline{F}_i &= -\frac{1}{V_o\epsilon_o} \sum_{\underline{k} \neq \underline{0}}^{\infty} i\underline{k} A(k) \sum_j^N F_{ji}(\underline{k}) \exp(-i\underline{k} \cdot \underline{r}_{ji}) \\ &\quad - \frac{1}{4\pi\epsilon_o} \sum_{\ell}^4 \sum_{j \neq i}^{\infty} \left\{ G_{ji}^\ell(\underline{r}_{ji}) B_{\ell+1}(r_{ji}) \underline{r}_{ji} + B_\ell(r_{ji}) \hat{\nabla}_i G_{ji}^\ell(\underline{r}_{ji}) \right\}. \end{aligned} \quad (52)$$

Where the scalar functions $A(k)$, $B_\ell(u)$, $F_{ji}(\underline{k})$ and $G_{ji}^\ell(\underline{u})$ are defined in equations 37 to 42, and the *vector* functions $\hat{\underline{V}}_i G_{ji}^\ell(\underline{r}_{ji})$ are as follows

$$\hat{\underline{V}}_i G_{ji}^0(\underline{r}_{ji}) = 0 \quad (53)$$

$$\hat{\underline{V}}_i G_{ji}^1(\underline{r}_{ji}) = C_i \underline{D}_j - C_j \underline{D}_i \quad (54)$$

$$\begin{aligned} \hat{\underline{V}}_i G_{ji}^2(\underline{r}_{ji}) = & -2C_j \underline{Q}_{\underline{j}} \cdot \underline{r}_{ji} - 2C_i \underline{Q}_{\underline{j}} \cdot \underline{r}_{ji} + 2\underline{Q}_{\underline{j}} \cdot \underline{D}_i - 2\underline{Q}_{\underline{i}} \cdot \underline{D}_j + \\ & \underline{Q}_{\underline{j}} : \underline{I} \underline{D}_i - \underline{Q}_{\underline{i}} : \underline{I} \underline{D}_j + (\underline{D}_j \cdot \underline{r}_{ji}) \underline{D}_i + (\underline{D}_i \cdot \underline{r}_{ji}) \underline{D}_j \end{aligned} \quad (55)$$

$$\begin{aligned} \hat{\underline{V}}_i G_{ji}^3(\underline{r}_{ji}) = & -2(\underline{D}_i \cdot \underline{r}_{ji}) \underline{Q}_{\underline{j}} \cdot \underline{r}_{ji} + 2(\underline{D}_j \cdot \underline{r}_{ji}) \underline{Q}_{\underline{i}} \cdot \underline{r}_{ji} + 2(\underline{Q}_{\underline{i}} : \underline{I}) \underline{Q}_{\underline{j}} \cdot \underline{r}_{ji} + 2(\underline{Q}_{\underline{j}} : \underline{I}) \underline{Q}_{\underline{i}} \cdot \underline{r}_{ji} \\ & + 4(\underline{Q}_{\underline{i}} \cdot \underline{Q}_{\underline{j}} + \underline{Q}_{\underline{j}} \cdot \underline{Q}_{\underline{i}}) \cdot \underline{r}_{ji} + (\underline{Q}_{\underline{i}} : \underline{R}_{\underline{j}i}) \underline{D}_j - (\underline{Q}_{\underline{j}} : \underline{R}_{\underline{i}i}) \underline{D}_i \end{aligned} \quad (56)$$

$$\hat{\underline{V}}_i G_{ji}^4(\underline{r}_{ji}) = -2(\underline{Q}_{\underline{i}} : \underline{R}_{\underline{j}i}) \underline{Q}_{\underline{j}} \cdot \underline{r}_{ji} - 2(\underline{Q}_{\underline{j}} : \underline{R}_{\underline{i}i}) \underline{Q}_{\underline{i}} \cdot \underline{r}_{ji} \quad (57)$$

5 The Torque on a Multipole

The torque acting on a point multipole in a lattice of point multipoles is obtained by applying the torque operator (20) to the potential according to the prescription given in (19).

$$\begin{aligned} \underline{T}_i = & \frac{1}{V_o \epsilon_o} \sum_{\underline{k} \neq \underline{0}}^{\infty} A(k) \sum_j^N \underline{F}_{ji}(\underline{k}) \exp(-i\underline{k} \cdot \underline{r}_{ji}) \\ & + \frac{1}{4\pi \epsilon_o} \sum_{\ell}^4 \sum_{j \neq i}^{\infty} B_\ell(r_{ji}) \underline{G}_{ji}^\ell(\underline{r}_{ji}). \end{aligned} \quad (58)$$

Where the scalar functions $A(k)$ and $B_\ell(u)$ are as above and $\underline{F}_{ji}(\underline{k})$ and $\underline{G}_{ji}^\ell(\underline{u})$ are now vector functions with the following forms:

$$\underline{F}_{ji}(\underline{k}) = (C_j - i\underline{k} \cdot \underline{D}_j \cdot -\underline{Q}_{\underline{j}} : \underline{K})(i\underline{k} \times \underline{D}_i - 2\underline{K} \times \underline{Q}_{\underline{i}}) \quad (59)$$

$$\underline{G}_{ji}^1(\underline{r}_{ji}) = C_j (\underline{r}_{ji} \times \underline{D}_i) + \underline{D}_j \times \underline{D}_i \quad (60)$$

$$\begin{aligned} \underline{G}_{ji}^2(\underline{r}_{ji}) = & 2C_j \underline{R}_{\underline{j}i} \times \underline{Q}_{\underline{i}} - (\underline{D}_j \cdot \underline{r}_{ji}) \underline{r}_{ji} \times \underline{D}_i + 2\underline{\Delta}_{\underline{j}i} \times \underline{Q}_{\underline{i}} + 2\underline{\Delta}_{\underline{j}i}^\dagger \times \underline{Q}_{\underline{i}} \\ & - 2(\underline{Q}_{\underline{j}} \cdot \underline{r}_{ji}) \times \underline{D}_i - (\underline{Q}_{\underline{j}} : \underline{I}) \underline{r}_{ji} \times \underline{D}_i + 4\underline{Q}_{\underline{j}} \times \underline{Q}_{\underline{i}} \end{aligned} \quad (61)$$

$$\begin{aligned} \underline{G}_{ji}^3(\underline{r}_{ji}) = & (\underline{Q}_{\underline{j}} : \underline{R}_{\underline{j}i}) \underline{r}_{ji} \times \underline{D}_i - 2(\underline{D}_j \cdot \underline{r}_{ji}) \underline{R}_{\underline{j}i} \times \underline{Q}_{\underline{i}} - 2(\underline{Q}_{\underline{j}} : \underline{I}) \underline{R}_{\underline{j}i} \times \underline{Q}_{\underline{i}} \\ & - 4\underline{\Theta}_{\underline{j}i} \times \underline{Q}_{\underline{i}} - 4\underline{\Theta}_{\underline{j}i}^\dagger \times \underline{Q}_{\underline{i}} \end{aligned} \quad (62)$$

$$\underline{G}_{ji}^4(\underline{r}_{ji}) = 2(\underline{Q}_{\underline{j}} : \underline{R}_{\underline{j}i}) \underline{R}_{\underline{j}i} \times \underline{Q}_{\underline{i}}, \quad (63)$$

in which the superscript † indicates a matrix transpose (which of course does not mean interchanging the indices i and j).

6 Comments on Application

The application of the above formulae to molecular dynamics work is not trivial (though it is easier than the formulae may suggest!). I therefore offer the following comments to guide the would-be user.

1. These formulae are available in FORTRAN source form in the CCP5 program library. The subroutines EWALD1 and EWALD2 contain the code for the reciprocal-space and real-space parts respectively. Coding of the self-interaction correction is found in EWALD1. Also available is the molecular dynamics program MDMULP, which uses these routines to simulate rigid molecules.
2. The formulae above include the calculation of the torque on each multipole. This is appropriate if the multipole sits at the molecule centre of mass, but in practice this may not be the case. It is then required to translocate the effect of this torque from the site of the multipole to the centre of mass. A method for doing this is described in a CCP5 Newsletter article [4]. Alternatively, a shift theorem may be used to redefine the multipole at the centre of mass. This is the strategy adopted by the program MDMULP.
3. Correct use of the Ewald summation requires specification of the Ewald convergence parameter ξ and an appropriate cut-off in both real and reciprocal space. A simple, practical way of optimising these parameters is to take the starting configuration and proceed as follows:
 - (a) Choose the real-space cutoff (r_{cut}) compatible with the size of simulation cell,
 - (b) Set a preliminary reciprocal space cut-off ($k_{max} = 15 * 2\pi/L$, say),
 - (c) Calculate the potential energy of the system over a range of values of ξ in steps of about 0.1\AA^{-1} until the potential energy shows signs of converging. (i.e. a plateau appears in the energy *vs.* ξ plot.) A single step MD run is sufficient for this.
 - (d) Use the smallest value of ξ giving a converged result for subsequent simulations.
 - (e) Try reducing the value of k_{max} as far as possible, without affecting the convergence. Use the smallest safe value for subsequent simulations.

This procedure will give a reasonably optimised set of parameters for the Ewald method. Beware that the starting configuration is reasonably representative of the simulation to be undertaken e.g. if a lattice is used to as the starting configuration, make sure the multipoles are randomly orientated.

4. Users of this method should note that the definition of the quadrupole in this article is based on the form

$$Q^{\alpha\beta} = \frac{1}{2} \sum_{k=1}^n q_k r_k^\alpha r_k^\beta. \quad (64)$$

This is not the form that is commonly encountered in the literature. The matrix \underline{Q} used here is, strictly speaking, the *second moment* of the charge distribution. The standard multipole $\underline{\underline{Q}}$ can be obtained from \underline{Q} this via the relation:

$$Q^{\alpha\beta} = 3 Q^{\alpha\beta} - \delta_{\alpha\beta} Tr \underline{Q} \quad (65)$$

where $Tr \underline{Q}$ is the sum of the diagonal elements of \underline{Q} . Matrix $\underline{\underline{Q}}$ is the so-called *traceless* multipole. It is not possible to convert from $\underline{\underline{Q}}$ to \underline{Q} unless the trace of \underline{Q} is known beforehand.

5. Finally, it is important to note that this method requires that the multipoles be defined with respect to the *laboratory frame* and as a result the multipole components change as the molecules rotate in space. Recalculation of the rotated multipole is accomplished using the standard rotation matrix. i.e. if

$$\underline{r}^{\circ} = \underline{R} \underline{r} \quad (66)$$

where \underline{r}° is a vector in the body frame of reference, \underline{r} is the corresponding vector in the laboratory frame and \underline{R} is the rotation matrix, then:

$$\underline{D} = \underline{R}^{\dagger} \underline{D}^{\circ} \quad (67)$$

and

$$\underline{\underline{Q}} = \underline{R}^{\dagger} \underline{\underline{Q}}^{\circ} \underline{R}. \quad (68)$$

In these formulae the superscript $^{\circ}$ indicates the body frame of reference and † indicates a matrix transpose.

7 Conclusion

The multipole Ewald summation in Cartesian form is derived using appropriate multipole operators, which act on the corresponding expression for a lattice of unit point charges. The forces and torques acting on a multipole are calculated in a similar manner. The self interaction correction is obtained by isolating the terms in real space which correspond to the classical multipole-multipole self interaction and removing the point-multipole contributions.

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Appendix: Properties of the $B_\ell(u)$ Functions

The lowest order $B_\ell(u)$ functions is

$$B_0(u) = \frac{1}{u} \operatorname{erfc}(\xi u) \quad (69)$$

where

$$\operatorname{erfc}(\xi u) = \frac{2}{\sqrt{\pi}} \int_{\xi u}^{\infty} \exp(-s^2) ds. \quad (70)$$

It is convenient also to define the recursion relation

$$B_\ell(u) = \frac{1}{u^2} \left\{ (2\ell - 1) B_{\ell-1}(u) + \frac{(2\xi^2)^\ell}{\xi\sqrt{\pi}} \exp(-\xi^2 u^2) \right\}, \quad (71)$$

which is obtained for $\ell > 0$ by repeated differentiation of $B_0(u)$ with respect to u , as is easily proven by induction.

If the scalar variable u is defined to be

$$u = |\underline{r}_j - \underline{r}_g| = [(x_j - x_g)^2 + (y_j - y_g)^2 + (z_j - z_g)^2]^{1/2} \quad (72)$$

(in keeping with the rôle of u in the equations above), then it is easily shown that for $r^\alpha, r^\beta = x, y, z$ etc.

$$\frac{\partial}{\partial r_g^\alpha} B_\ell(r_{jg}) = (r_j^\alpha - r_g^\alpha) B_{\ell+1}(r_{jg}) \quad (73)$$

$$\frac{\partial^2}{\partial r_g^\alpha \partial r_g^\beta} B_\ell(r_{jg}) = (r_j^\alpha - r_g^\alpha)(r_j^\beta - r_g^\beta) B_{\ell+2}(r_{jg}) - \delta_{\alpha\beta} B_{\ell+1}(r_{jg}) \quad (74)$$

From these results it follows that

$$\hat{\nabla} B_\ell(r_{jg}) = (\underline{r}_j - \underline{r}_g) B_{\ell+1}(r_{jg}) \quad (75)$$

$$\hat{\underline{\Omega}} B_\ell(r_{jg}) = \underline{R}_{jg} B_{\ell+2}(r_{jg}) - \underline{I} B_{\ell+1}(r_{jg}). \quad (76)$$

These relationships are used throughout the derivations above.

The expansion (46) used in the derivation of the self interaction energy is obtained using the following series expansions

$$\frac{1}{u} \operatorname{erfc}(\xi u) = \frac{1}{u} - \frac{2\xi}{\sqrt{\pi}} \left\{ 1 - \frac{(\xi u)^2}{3} + \frac{(\xi u)^4}{10} - \frac{(\xi u)^6}{42} + \frac{(\xi u)^8}{216} - \dots \right\} \quad (77)$$

$$\exp(\xi^2 u^2) = 1 - (\xi u)^2 + \frac{(\xi u)^4}{2} - \frac{(\xi u)^6}{6} + \frac{(\xi u)^8}{24} - \dots \quad (78)$$

which are obtained by direct differentiation using Maclaurin's formula.

Combining these expansions in the recursion relation (71) and collecting like powers in u allows the following expansions to be produced.

$$B_0(u) = \frac{1}{u} - \frac{2\xi}{\sqrt{\pi}} + O(u) \quad (79)$$

$$B_1(u) = \frac{1}{u^3} - \frac{4\xi^3}{3\sqrt{\pi}} + O(u) \quad (80)$$

$$B_2(u) = \frac{3}{u^5} - \frac{8\xi^5}{5\sqrt{\pi}} + O(u) \quad (81)$$

$$B_3(u) = \frac{15}{u^7} - \frac{16\xi^7}{7\sqrt{\pi}} + O(u) \quad (82)$$

$$B_4(u) = \frac{105}{u^9} - \frac{32\xi^9}{9\sqrt{\pi}} + O(u) \quad (83)$$

etc. Or in general

$$B_\ell(u) = \frac{(2\ell)!}{\ell!2^\ell u^{2\ell+1}} - \frac{(2\xi^2)^{\ell+1}}{(2\ell+1)\xi\sqrt{\pi}} + O_\ell(u) \quad (84)$$

where $O(u)$ represents terms of ascending powers of u (i.e. u^n with $n \geq 1$).

References

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