POINT MULTIPOLES IN THE EWALD SUMMATION

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Preamble

The purpose of this paper is to outline one possible treatment of point multipoles in an Ewald Summation. A point multipole in this application is considered to consist of a superimposed point charge, point dipole and point quadrupole; as might be obtained from an arbitrary charge distribution resolved into these components. The physical quantities described are the potential, force and torque experienced by a point multipole in an infinite system of repeating unit cells containing irregularly spaced multipoles.

The Multipole Operators

Taylor's expansion for a scalar function of several variables (i.e. $F(x_1, x_2, x_3, \dots)$ or $F(\underline{r})$) may be written as:

$$F(\underline{r} + \delta\underline{r}) = F(\underline{r}) + \delta\underline{r}\cdot\underline{\nabla}F(\underline{r}) + \underline{\underline{U}}:[\underline{\nabla\nabla}]F(\underline{r}) + \dots \text{ etc.} \qquad (1)$$

Where the matrix $\underline{\underline{U}}$ is defined by $U_{ij} = 1/2x_ix_j$ etc.
and the matrix $[\underline{\nabla\nabla}]$ is defined by $[\nabla\nabla]_{ij} = \frac{\partial^2}{\partial x_i\,\partial x_j}$ etc.

The operation indicated as : is the dyadic scalar product of the matrices (i.e. $\underline{\underline{A}}:\underline{\underline{B}} = A_{11}B_{11} + A_{12}B_{12} + \dots$ etc.). (The terms of the series (1) can be regarded as a series consisting of consecutive contractions of tensors of rank 0,1,2, ... etc. to give a scalar result.)

The electrostatic potential at a point $\underline{r}$ due to a multipole at the origin and consisting of n point charges at the points $\{\underline{r}_k\}$ is given by (2). (Where the vectors $\underline{r}_k$ specify the positions of the charges q_k with respect to the adopted origin of the multipole. For our purposes the adopted origin may be taken as the centre of the charge distribution. The position of the multipole in space is thus regarded as the position of its adopted centre.)

$$V(\underline{r}) = \frac{1}{4\pi\varepsilon_0} \sum_{k=1}^{n} \frac{q_k}{|\underline{r}-\underline{r}_k|} \tag{2}$$

If we assume that the spatial size of the multipole is minute in relation to r (i.e. $r \gg r_k$) we may use Taylor's expansion of $1/r$ with (2) to obtain the following expression for $V(\underline{r})$ (in which we ignore contributions above quadrupole).

$$V(r) = \frac{1}{4\pi\varepsilon_0} \left\{c_a - \underline{d}_a \cdot \underline{\nabla} + \underline{\underline{Q}}_a : [\nabla\nabla]\right\} \frac{1}{r} \tag{3}$$

Where: $c_a = \sum_{k=1}^{n} q_k$ is the multipole net charge

$\underline{d}_a = \sum_{k=1}^{n} q_k \underline{r}_k$ is the multipole net dipole

$\underline{\underline{Q}}_a = \sum_{k=1}^{n} q_k \underline{\underline{U}}_k$ is the multipole net quadrupole

If we define the terms in the brackets of (3) to be an operator $\hat{M}_a$ we may rewrite (3) as:

$$V(r) = \hat{M}_a (4\pi\varepsilon_0 r)^{-1} \tag{4}$$

From which we see that the potential due to a point multipole is obtained by applying the operator $\hat{M}_a$ to the expression describing the potential due to a unit positive charge.

By a similar reasoning we may deduce that the potential ϕ_b of a second

402ABO

point multipole due to the potential field $V(\underline{r})$ of the first, is given by:

$$\Phi_b = \hat{M}_b\, V(r) \quad (\text{or } \hat{M}_b \hat{M}_a (4\pi\varepsilon_o r)^{-1}) \tag{5}$$

Where $\hat{M}_b = c_b + \underline{d}_b \cdot \underline{\nabla} + \underline{\underline{Q}}_b : [\underline{\nabla\nabla}]$ (6)

The force acting on the second multipole will be given by applying the operator $-\underline{\nabla}_b$ to the expression (5) in the usual manner. Thus

$$\underline{F}_b = -\underline{\nabla}_b \hat{M}_b \hat{M}_a (4\pi\varepsilon_0 r)^{-1} \tag{7}$$

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

$$\underline{T}_b = -\sum_{k=1}^{n} q_k \underline{r}_k \times \underline{\nabla} V(\underline{r} + \underline{r}_k) \tag{8}$$

From which we may deduce that

$$\underline{T}_b = -\left\{\underline{d}_b \times \underline{\nabla} + 2\underline{\underline{Q}}_b * [\underline{\nabla\nabla}]\right\} V(\underline{r}) \tag{9}$$

and so obtain the torque operator $\hat{L}_b$ as:

$$\hat{L}_b = -\left\{\underline{d}_b \times \underline{\nabla} + \underline{\underline{Q}}_b * [\nabla\nabla]\right\} \tag{10}$$

(The operation implied by * is a vector product of the matrices on either side; according to the recipe:

If $\underline{V} = \underline{\underline{A}} * \underline{\underline{B}}$ then for matrices of dimension 3

$$V_i = \sum_j^m (A_{i+1,j} B_{i+2,j} - A_{i+2,j} B_{i+1,j}) \tag{11}$$

Where the indices follow a cyclic progression (i.e. if i=2 then i+1 ≡3, i+2 ≡1. If i=3 then i+1 ≡1, i+2 ≡2 etc.))

The Ewald Summation

The potential at a point $\underline{r}$ (not at a lattice site) in an infinite periodic lattice of unit point charges is given by the Ewald Summation[1,2] as:-

$$V_{\Sigma}(\underline{r}) = \frac{1}{V_0\varepsilon_0}\sum_{k\neq 0}^{\infty}\sum_{j}^{n} A_k \exp(-i\underline{k}.(\underline{r}_j - \underline{r})) + \frac{1}{4\pi\varepsilon_0}\sum_{j}^{\infty} B_0(|\underline{r}_j - \underline{r}|) \quad (12)$$

where $A_k = \exp(-k^2/4\alpha^2)/k^2$

$B_0(u) = \mathrm{erfc}(\alpha u)/u$

n = number of point charges in unit cell

α = Ewald's convergence parameter

V_0 = volume of unit cell

$\underline{k}$ = reciprocal lattice vector (e.g. $\underline{k} = \frac{2\pi}{L}(n_a,n_b,n_c)$ for a cubic system

k = index of $\underline{k}$ vector

According to the principles outlined in the previous section we may adapt equation (12) to suit a lattice of point multipoles by applying the set of operators $\hat{M}_j$ defined by:

$$\hat{M}_j = c_j - \underline{d}_j.\underline{\nabla} + \underline{\underline{Q}}_j:[\underline{\nabla\nabla}] \quad (13)$$

Following this prescription we obtain the expression

$$V(r) = \frac{1}{V_0\varepsilon_0}\sum_{k\neq 0}^{\infty}\sum_{j}^{n} (c_j - i\underline{d}_j.\underline{k} - \underline{\underline{Q}}_j:[\underline{kk}])A_k\exp(-i\underline{k}.(\underline{r}_j - \underline{r}))$$

$$+ \frac{1}{4\pi\varepsilon_0}\sum_{j}^{\infty} (c_j B_0(|\underline{r}_j - \underline{r}|) - (\underline{d}_j.(\underline{r}_j - \underline{r}) + \underline{\underline{Q}}_j:\underline{\underline{I}})B_1(|\underline{r}_j - \underline{r}|)$$

$$+ \underline{\underline{Q}}_j:[(\underline{r}_j - \underline{r})(\underline{r}_j - r)]B_2(|\underline{r}_j - \underline{r}|)) \quad (14)$$

Where $:[\underline{kk}]$ is a matrix formed from the products $k_i k_j$ etc. $[(\underline{r}_j-\underline{r})(\underline{r}_j-\underline{r})]$ is a matrix formed from the products $(x_j-x)(y_j-y)$ etc.

$B_1(|\underline{r}_j - \underline{r}|) \ldots B_\ell(|\underline{r}_j - \underline{r}|)$ are a series of functions derived from $B_0(|\underline{r}_j - \underline{r}|)$ according to the recursion relation:

$$B_\ell(u) = \frac{1}{u^2}\left\{(2\ell - 1)B_{\ell-1}(u) + \frac{(2\alpha^2)^\ell}{\alpha\sqrt{\pi}}\exp(-\alpha^2u^2)\right\} \qquad (15)$$

Further important properties of the functions $B_\ell(|\underline{r}_j - \underline{r}|)$ are given in the appendix.

Equation (14) describes the potential field due to a lattice of point multipoles. The potential energy of a 'guest' multipole at position $\underline{r}$ is given by applying the operator $\hat{M}_g$ to equation (14) where:

$$M_g = c_g + \underline{d}_g.\underline{\nabla} + \underline{\underline{Q}}_g:[\underline{\nabla\nabla}] \qquad (16)$$

The result of this operation being:

$$\phi_g = \frac{1}{V_0\varepsilon_0}\sum_{k\neq 0}^{\infty}\sum_{j}^{n} A_k F_{kjg}\exp(-i\underline{k}.(\underline{r}_j - \underline{r})) + \frac{1}{4\pi\varepsilon_0}\sum_{\ell=0}^{4}\sum_{j}^{\infty} B_\ell(|\underline{r}_j - \underline{r}|)G_{\ell jg}$$

(17)

Where the functions A_k and B_ℓ have already been described. The functions F_{kjg} and $G_{\ell jg}$ are as follows:

$$F_{kjg} = (c_g + i\underline{d}_g.\underline{k} - \underline{\underline{Q}}_g:[\underline{kk}])(c_j - i\underline{d}_j.\underline{k} - \underline{\underline{Q}}_j:[\underline{kk}]) \qquad (18)$$

$$
\left.
\begin{aligned}
G_{ojg} &= c_g c_j \\
G_{1jg} &= \underline{d}_g\cdot(\underline{r}_j - \underline{r})c_j - \underline{d}_j\cdot(\underline{r}_j - \underline{r})c_g - \underline{\underline{Q}}_g:\underline{\underline{I}}c_j - \underline{\underline{Q}}_j:\underline{\underline{I}}c_g + \underline{d}_g\cdot\underline{d}_j \\
G_{2jg} &= \underline{\underline{Q}}_g:[(\underline{r}_j - \underline{r})(\underline{r}_j - \underline{r})]c_j + \underline{\underline{Q}}_j:[(\underline{r}_j - \underline{r})(\underline{r}_j - \underline{r})]c_g \\
&\quad - \underline{d}_g\cdot(\underline{r}_j - \underline{r})\underline{d}_j\cdot(\underline{r}_j - \underline{r}) + 2\underline{\underline{Q}}_g:[\underline{d}_j(\underline{r}_j - \underline{r})] \\
&\quad - 2\underline{\underline{Q}}_j:[\underline{d}_g(\underline{r}_j - \underline{r})] + \underline{d}_j\cdot(\underline{r}_j - \underline{r})\underline{\underline{Q}}_g:\underline{\underline{I}} - \underline{d}_g\cdot(\underline{r}_j - \underline{r})\underline{\underline{Q}}_j:\underline{\underline{I}} \\
&\quad + 2\underline{\underline{Q}}_g:\underline{\underline{Q}}_j + \underline{\underline{Q}}_g:\underline{\underline{I}}\underline{\underline{Q}}_j:\underline{\underline{I}} \\
G_{3jg} &= \underline{d}_g\cdot(\underline{r}_j - \underline{r})\underline{\underline{Q}}_j:[(\underline{r}_j - \underline{r})(\underline{r}_j - \underline{r})] - \underline{d}_j\cdot(\underline{r}_j - \underline{r})\underline{\underline{Q}}_g:[(\underline{r}_j - \underline{r})(\underline{r}_j - \underline{r})] \\
&\quad - 4\underline{\underline{Q}}_g:[(\underline{r}_j - \underline{r})(\underline{\underline{Q}}_j\cdot(\underline{r}_j - \underline{r}))] \\
&\quad - \underline{\underline{Q}}_g:\underline{\underline{I}}\underline{\underline{Q}}_j:[(\underline{r}_j - \underline{r})(\underline{r}_j - \underline{r})] - \underline{\underline{Q}}_j:\underline{\underline{I}}\underline{\underline{Q}}_g:[(\underline{r}_j - \underline{r})(\underline{r}_j - \underline{r})] \\
G_{4jg} &= \underline{\underline{Q}}_g:[(\underline{r}_j - \underline{r})(\underline{r}_j - \underline{r})]\underline{\underline{Q}}_j:[(\underline{r}_j - \underline{r})(\underline{r}_j - \underline{r})]
\end{aligned}
\right\} \quad (19)
$$

In the usual situation we wish to evaluate the potential, not of a guest multipole, but of one of the multipoles at a lattice site. We can adapt the formulae (17) to (19) to this circumstance in the following way.

(i) We must extract from the equation (17) all those terms involving both the guest multipole (index 'g') and the multipole at the lattice site of interest (index 'i'). These terms will call for special treatment later.

(ii) In the other terms we simply set the index 'g' to index 'i' and replace $\underline{r}$ by $\underline{r}_i$. Thus as far as these terms are concerned, the guest multipole and the 'ith' multipole are one and the same.

If we now examine the terms separated out from (17) according to (i) above, it is clear that if we are to regard the guest multipole as being the 'i^{th}' multipole, then these terms represent a 'self-interaction' energy, which physically is zero, but mathematically is indeterminate. We may choose simply to exclude these terms from our summation (i.e. set them to zero) but computationally it is more convenient to proceed otherwise.

If we consider the second group of terms on the right of equation (17) and obtain those terms in which both indices 'i' and 'g' appear we will have

$$\frac{1}{4\pi\varepsilon_0} \sum_{\ell=0}^{4} B_\ell(|r_i - r|)G_{\ell ig} \tag{20}$$

It is clear from the definition of the functions $B_\ell(u)$ in equations (12) and (15) that this term becomes indeterminate when we equate $\underline{r}$ and $\underline{r}_i$. If however we expand these functions as polynomials in the argument u (see Appendix) we obtain in place of (20):

$$\frac{1}{4\pi\varepsilon_0} \sum_{\ell=0}^{4} \left\{ \frac{(2\ell)!\ G_{\ell ig}}{\ell!\, 2^\ell\ u^{2\ell+1}} - \frac{(2\alpha^2)^{\ell+1}\ G_{\ell ig}}{(2\ell+1)\,\alpha\pi^{1/2}} + G_{\ell ig} O_\ell(u) \right\} \tag{21}$$

Where $O_\ell(u)$ represents a sum of terms in u and higher powers of u.

If we now examine the first term of the expansion (21) we are able to equate this term with the conventional (or non-Ewald) description of the potential energy function of two multipoles separated by a distance u. As u tends to zero (i.e. as $\underline{r}_i$ and $\underline{r}$ merge) it is this term that becomes indeterminate. Because of its identity with the conventional potential expression we may simply remove this term altogether (knowing it to be physically zero). We also see that the terms $O_\ell(u)$ necessarily become zero as u tends to zero. Thus the only surviving term is:

$$- \frac{1}{4\pi\varepsilon_0} \sum_{\ell=0}^{4} \frac{(2\alpha^2)^{\ell+1} G_{\ell ii}}{(2\ell+1)\alpha\pi^{1/2}} \qquad (22)$$

Two further comments are in order. Firstly it can be seen from the identities (19) that within the $G_{\ell ii}$ functions themselves many of the terms are zero because of their dependence on $(\underline{r}_i - \underline{r})$, which is zero in this circumstance. Secondly, because of the identification of the first term of the expansion (21) with the conventional potential energy expression, we can be sure that the term (22) represents a complete correction of equation (17) to the case where the guest multipole is at a lattice site. (Note that this also means that we may simply use the index substitution 'g' → 'i' in the Fourier component of (17) without further complication.) Thus we may write:

$$\phi_i = \frac{1}{V_0\varepsilon_0} \sum_{k\neq 0}^{\infty} \sum_{j}^{n} A_k F_{kji} \exp(-i\underline{k}.(\underline{r}_j - \underline{r}_i))$$

$$+ \frac{1}{4\pi V_0\varepsilon_0} \sum_{\ell\neq 0}^{4} \sum_{j\neq i}^{\infty} B_\ell(|\underline{r}_j - \underline{r}_i|) G_{\ell ji} + C \qquad (23)$$

Where the constant C may be derived from (22) and is:

$$C = \frac{-2\alpha}{4\pi^{3/2}\varepsilon_0} \left\{ c_i^{\,2} + 2\alpha^2 \left\{ \frac{1}{3} (2\underline{\underline{Q}}_i : \underline{\underline{I}} c_i + d_i^{\,2}) + \frac{2\alpha^2}{5} (2\underline{\underline{Q}}_i : \underline{\underline{Q}}_i + (\underline{\underline{Q}}_i : \underline{\underline{I}})^2) \right\} \right\} \qquad (24)$$

It is worth noting at this point that if all the dipoles and quadrupoles are set to zero, this expression will reduce to standard Ewald form for a lattice of point changes[1,2]. Also if the charges and quadrupoles are set to zero, the result is the Kornfeld expression for a lattice of point dipoles as described by Adams and McDonald[3]. The proof of these statements is left as an exercise for the intrepid reader.

The force acting on the 'i^{th}' multipole in a lattice of multipoles is obtained by applying the operator $-\underline{\nabla}_i$ to equation (23). The result is:

$$\underline{F}_i = \frac{-1}{V_0\varepsilon_0}\sum_{k\neq 0}^{\infty}\sum_{j}^{n} i\underline{k}A_k F_{kji}\exp(-i\underline{k}\cdot(\underline{r}_j - \underline{r}_i))$$

$$-\frac{1}{4\pi\varepsilon_0}\sum_{\ell=0}^{4}\sum_{j\neq i}^{\infty} G_{\ell ji}B_{\ell+1}(|\underline{r}_j - \underline{r}_i|)(\underline{r}_j - \underline{r}_i) + B_{\ell}(|\underline{r}_j - \underline{r}_i|)\underline{\nabla}_i G_{\ell ji} \qquad (25)$$

Where the functions A_k, F_{kji}, $G_{\ell ji}$ and B_{ℓ} have been encountered already. The vector functions $\underline{\nabla}_i G_{\ell ji}$ however, are as follows:

$$\left.\begin{aligned}
\underline{\nabla}_i G_{0ji} &= 0 \\
\underline{\nabla}_i G_{1ji} &= c_i\underline{d}_j - c_j\underline{d}_i \\
\underline{\nabla}_i G_{2ji} &= -\,2c_i\underline{\underline{Q}}_j\cdot(\underline{r}_j - \underline{r}_i) - 2c_j\underline{\underline{Q}}_i\cdot(\underline{r}_j - \underline{r}_i) \\
&\quad + \underline{d}_i\cdot(\underline{r}_j - \underline{r}_i)\underline{d}_j + \underline{d}_j\cdot(\underline{r}_j - \underline{r}_i)\underline{d}_i \\
&\quad + 2\underline{\underline{Q}}_j\cdot\underline{d}_i + \underline{\underline{Q}}_j\underline{\underline{I}}\underline{d}_i - 2\underline{\underline{Q}}_i\cdot\underline{d}_j - \underline{\underline{Q}}_i:\underline{\underline{I}}\underline{d}_j \\
\underline{\nabla}_i G_{3ji} &= \underline{\underline{Q}}_i:[(\underline{r}_j - r_i)(\underline{r}_j - \underline{r}_i)]\underline{d}_j + 2\underline{d}_j\cdot(\underline{r}_j - \underline{r}_i)\underline{\underline{Q}}_i\cdot(\underline{r}_j - \underline{r}_i) \\
&\quad - \underline{\underline{Q}}_j:[(\underline{r}_j - \underline{r}_i)(\underline{r}_j - \underline{r}_i)]\underline{d}_i - 2\underline{d}_i\cdot(\underline{r}_j - \underline{r}_i)\underline{\underline{Q}}_j\cdot(r_j - \underline{r}_i) \\
&\quad + 4(\underline{\underline{Q}}_i\cdot\underline{\underline{Q}}_j + \underline{\underline{Q}}_j\cdot\underline{\underline{Q}}_i)\cdot(\underline{r}_j - \underline{r}_i) + 2\underline{\underline{Q}}_i\cdot\underline{\underline{I}}\underline{\underline{Q}}_j\cdot(\underline{r}_j - \underline{r}_i) \\
&\quad + 2\underline{\underline{Q}}_j:\underline{\underline{I}}\underline{\underline{Q}}_i\cdot(\underline{r}_j - \underline{r}_i) \\
\underline{\nabla}_i G_{4ji} &= -\,2\underline{\underline{Q}}_i:[(\underline{r}_j - \underline{r}_i)(\underline{r}_j - \underline{r}_i)]\underline{\underline{Q}}_j\cdot(\underline{r}_j - \underline{r}_i) \\
&\quad - 2\underline{\underline{Q}}_j:[(\underline{r}_j - \underline{r}_i)(\underline{r}_j - \underline{r}_i)]\underline{\underline{Q}}_i\cdot(\underline{r}_j - \underline{r}_i)
\end{aligned}\right\} \qquad (26)$$

To determine the torque acting on a point multipole at a lattice site, we must apply an operator $\hat{L}_i$ analogous to that presented in (10) to the potential field equation given in (14) and proceed in a similar manner to that which produced the result (23). In this case however the result is:

$$\underline{T}_i = \frac{1}{V_0 \varepsilon_0} \sum_{k \neq 0}^{\infty} \sum_{j}^{n} A_k \underline{F}_{kji} \exp(-i\underline{k}.(\underline{r}_j - \underline{r}_i))$$

$$+ \frac{1}{4\pi\varepsilon_0} \sum_{\ell=1}^{4} \sum_{j \neq i}^{\infty} B_\ell(|\underline{r}_j - \underline{r}_i|)\underline{G}_{\ell ji} \qquad (27)$$

Where A_k and B_ℓ are the same functions as in the previous formulae. $\underline{F}_{kji}$ and $\underline{G}_{\ell ji}$ however are now vector functions of the following forms:

$$\underline{F}_{kji} = (-i\underline{d}_i \times \underline{k} + 2\underline{\underline{Q}}_i * [\underline{kk}])(c_j - i\underline{d}_j.\underline{k} - \underline{\underline{Q}}_j : [\underline{kk}]) \qquad (28)$$

$$\left.\begin{aligned}
\underline{G}_{1ji} &= - \underline{d}_i \times (\underline{r}_j - \underline{r}_i)c_j - \underline{d}_i \times \underline{d}_j \\
\underline{G}_{2ji} &= - 2\underline{\underline{Q}}_i * [(\underline{r}_j - \underline{r}_i)(\underline{r}_j - \underline{r}_i)]c_j + \underline{d}_i \times (\underline{r}_j - \underline{r}_i)\underline{d}_j.(\underline{r}_j - \underline{r}_i) \\
&\quad - 2\underline{\underline{Q}}_i * [\underline{d}_j(\underline{r}_j - \underline{r}_i)] - 2\underline{\underline{Q}}_i * [(\underline{r}_j - \underline{r}_i)\underline{d}_j] \\
&\quad + 2\underline{d}_i \times \underline{\underline{Q}}_j.(\underline{r}_j - \underline{r}_i) + \underline{d}_i \times (\underline{r}_j - \underline{r}_i)\underline{\underline{Q}}_j : \underline{\underline{I}} - 4\underline{\underline{Q}}_i * \underline{\underline{Q}}_j \\
\underline{G}_{3ji} &= - \underline{d}_i \times (\underline{r}_j - \underline{r}_i)\underline{\underline{Q}}_j : [(\underline{r}_j - \underline{r}_i)(\underline{r}_j - \underline{r}_i)] + 2\underline{d}_j.(\underline{r}_j - \underline{r}_i)\underline{\underline{Q}}_i * \\
&\qquad [(\underline{r}_j - \underline{r}_i)(\underline{r}_j - \underline{r}_i)] \\
&\quad + 4\underline{\underline{Q}}_i * ([(\underline{r}_j - \underline{r}_i)(\underline{\underline{Q}}_j.(\underline{r}_j - \underline{r}_i))] + [(\underline{\underline{Q}}_j.(\underline{r}_j - \underline{r}_i))(\underline{r}_j - \underline{r}_i)]) \\
&\quad + 2\underline{\underline{Q}}_i * [(\underline{r}_j - \underline{r}_i)(\underline{r}_j - \underline{r}_i)]\underline{\underline{Q}}_j : \underline{\underline{I}} \\
\underline{G}_{4ji} &= - 2\underline{\underline{Q}}_i * [(\underline{r}_j - r_i)(r_j - \underline{r}_i)]\underline{\underline{Q}}_j : [(\underline{r}_j - \underline{r}_i)(\underline{r}_j - \underline{r}_i)]
\end{aligned}\right\} \qquad (29)$$

It may be safely assumed from the complicated nature of these formulae, that these equations are difficult to program in an efficient manner.

However, it should be pointed out that the Fourier components of the formulae presented above are particularly elegant and straightforward and are little more difficult to program than would be the case in a system containing point charges only. Also, despite the cumbersome nature of the terms derived from the original complementary error function (i.e. the terms involving the B_ℓ functions) they are no more difficult to program than would be the case if the direct summation method were employed, provided that the B_ℓ functions are generated via the recursion relation (15). A primitive version of a program using these formulae is available from the author at Daresbury Laboratory.

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References

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3 D.J. Adams, I.R. McDonald, Molec. Phys. (1976) 32, 931.

Appendix: The B_ℓ Functions

We begin with the function $B_0(u)$:

$$B_0(u) = \frac{1}{u} \operatorname{erfc}(\alpha u) \qquad \text{(a)}$$

$$\text{Where: } \operatorname{erfc}(\alpha u) = \frac{2}{\pi^{1/2}} \int_{\alpha u}^{\infty} \exp(-s^2)ds \qquad \text{(b)}$$

We may also define the recursion relation:

$$B(u) = \frac{1}{u^2} \left\{(2\ell - 1)B_{\ell-1}(u) + \frac{(2\alpha^2)^\ell}{\alpha\pi^{1/2}} \exp(-\alpha^2 u^2)\right\} \quad (\ell > 0) \qquad \text{(c)}$$

If we define $u = |\underline{r}_j - \underline{r}| = \{((x_j)_1 - x_1)^2 + ((x_j)_2 - x_2)^2 + ((x_j)_3 - x_3)^2\}^{1/2}$,

then it is easily shown that:

$$\frac{\partial}{\partial x_r} B_\ell(u) = ((x_j)_r - x_r)B_{\ell+1}(u) \qquad (r = 1,2,3)$$

$$\frac{\partial^2}{\partial x_r \partial x_s} B_\ell(u) = ((x_j)_r - x_r)((x_j)_s - x_s)B_{\ell+2}(u) - \delta_{rs}B_{\ell+1}(u) \qquad (r,s = 1,2,3)$$

(d)

From which we obtain:

$$\underline{\nabla} B_\ell(u) = (\underline{r}_j - \underline{r})B_{\ell+1}(u)$$

$$[\underline{\nabla\nabla}]B_\ell(u) = [(\underline{r}_j - \underline{r})(\underline{r}_j - \underline{r})]B_{\ell+2}(u) - \underline{\underline{I}}\, B_{\ell+1}(u) \qquad \text{(e)}$$

These relationships are used throughout the derivations (14) to (29) of the previous sections.

To obtain the expansion (21) of the expression (20) we use the following series expansions:

$$\frac{1}{u}\operatorname{erfc}(\alpha u) = \frac{1}{u} - \frac{2\alpha}{\pi^{1/2}} \quad 1\left\{- \frac{(\alpha u)^2}{3} + \frac{(\alpha u)^4}{10} - \frac{(\alpha u)^6}{42} + \frac{(\alpha u)^8}{216} - \cdots\right\}$$

$$\exp(-\alpha^2 u^2) = 1 - (\alpha u)^2 + \frac{(\alpha u)^4}{2} - \frac{(\alpha u)^6}{6} + \frac{(\alpha u)^8}{24} - \cdots \qquad \text{(f)}$$

Combining the expansions (f) in the recursion relation (c) and collecting terms of like powers in u allows the following expansions of $B_\ell(u)$ to be produced.

$$B_0(u) = \frac{1}{u} - \frac{2\alpha}{\pi^{1/2}} + O(u)$$

$$B_1(u) = \frac{1}{u^3} - \frac{4\alpha^3}{3\pi^{1/2}} + O(u)$$

$$B_2(u) = \frac{3}{u^5} - \frac{8\alpha^5}{5\pi^{1/2}} + O(u)$$

$$B_3(u) = \frac{15}{u^7} - \frac{16\alpha^7}{7\pi^{1/2}} + O(u)$$

$$B_4(u) = \frac{105}{u^9} - \frac{32\alpha^9}{9\pi^{1/2}} + O(u)$$

etc. Or in general:

$$B_\ell(u) = \frac{(2\ell)!}{\ell!\,2^\ell u^{2\ell+1}} - \frac{(2\alpha^2)^{\ell+1}}{(2\ell+1)\,\alpha\pi^{1/2}} + O(u)$$

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