Charge - Charge Interactions

Assume Pair $\langle i, j \rangle$

1. Potential in Site i due to charge in site j

$$\phi(r) = \frac{q_j}{4\pi\varepsilon_0}\frac{1}{r}\left[1 - e^{-a\left(\frac{r}{A}\right)^4} + a^{1/4}\frac{r}{A}\,\Gamma\!\left(\tfrac{3}{4}\right) Q\!\left(\tfrac{3}{4}, a\left(\tfrac{r}{A}\right)^4\right)\right]$$

Where :

$A = (\alpha_i \alpha_j)^{\frac{1}{6}}$, $r \equiv r_{ij}$, $Q(a,x) = \Gamma(a,x) / \Gamma(a)$, $\Gamma(a,x) = \int_x^\infty t^{a-1} e^{-t}\,dt$, $\Gamma(a) = \int_0^\infty t^{a-1} e^{-t}\,dt$

* The development and obtention of this exprension is detailed in page 18 of the TTM notes document
* Q and Γ are tabulated functions.

See github.com/paesanilab/clusters/tree/master/pot/gammq.h for Q and Γ

See github.com/paesanilab/clusters/tree/master/pot/coulomb.h , function smear_ttm4x::smear01 for obtantion of ts∅ & ts1, which are the factors in front of the charge for the potential and electric field

$\phi_{i\leftarrow j}(r_{ij}) = ts\emptyset\, q_j$, where $ts\emptyset = \frac{1}{4\pi\varepsilon_0}\frac{1}{r}\left[1 - e^{-a\left(\frac{r}{A}\right)^4} + a^{1/4}\frac{r}{A}\,\Gamma\!\left(\tfrac{3}{4}\right) Q\!\left(\tfrac{3}{4}, a\left(\tfrac{r}{A}\right)^4\right)\right]$ Read: field in i due to j.

Note: Code seems to use scaled charges ($q/4\pi\varepsilon_0$)
Note: "a" is the smearing. For charge-charge, $a \equiv aCC = 0.4$

$E^{\hat{k}}_{i\leftarrow j} = +ts1\; q_j\; r^{\hat{k}}_{ij}$, where $ts1 = \frac{1}{4\pi\varepsilon_0}\frac{1}{r^3}\left(1 - e^{-a\left(\frac{r}{A}\right)^4}\right)$ coming from $\vec{E} = \frac{q}{4\pi\varepsilon_0}\frac{\vec{r}}{|r|^3}$

$E_{j\leftarrow i} = -ts1\; q_i\; r^{\hat{k}}_{ij}$

Polarizable Point Dipoles method: J. Chem. Phys., 133, 234101 (2010), Section II.

$$U_{el} = \boxed{U_{qq}} + \boxed{U_{q\mu}} + \boxed{U_{\mu\mu}} + \boxed{U_{dip}^{pol}} = \sum_i \sum_{j>i} \left(\boxed{q_i \hat{T}_{ij} q_j} + \boxed{\mu_i^\alpha \hat{T}_{ij}^\alpha q_j - q_i \hat{T}_{ij}^\alpha \mu_j^\alpha} \boxed{-\mu_i^\alpha T_{ij}^{\alpha\beta} \mu_j^\beta} \right) + \boxed{\frac{1}{2} \sum_{i=1}^{N_\mu} \vec{\mu}_i \cdot \hat{\alpha}_i^{-1} \cdot \vec{\mu}_i}$$

* $\hat{\alpha}$ is a scalar if i is isotropic. In our simulations, atoms are spherically symmetric, thus $\hat{\alpha}$ will always be a scalar.
* $T_{ij}^{(\alpha)(\beta)}$ are the electrostatic Tensors.
* q_i is the charge on site i, and $\mu_i^\alpha = \sum \mu_i^\alpha$, $\alpha = x, y, z$

The electrostatic tensors are defined as:

$$\hat{T}_{ij} = \left[S_0(r)\right] \frac{1}{r} \qquad \hat{T}_{ij}^\alpha = \nabla_\alpha \hat{T}_{ij} = -\left[S_1(r)\right] \frac{r_\alpha}{r^3} \qquad \hat{T}_{ij}^{\alpha\beta} = \nabla_\alpha \hat{T}_{ij}^\beta = \left[S_2(r)\right] \frac{3 r_\alpha r_\beta}{r^5} - \left[S_1(r)\right] \frac{\delta_{\alpha\beta}}{r^3}$$

$$\hat{T}_{ij}^{\alpha\beta\gamma} = \nabla_\alpha \hat{T}_{ij}^{\beta\gamma} = -\left[S_3(r)\right] \frac{15}{r^7} r_\alpha r_\beta r_\gamma + \left[S_2(r)\right] \frac{3}{r^5} \left(r_\alpha \delta_{\beta\gamma} + r_\beta \delta_{\alpha\gamma} + r_\gamma \delta_{\alpha\beta} \right)$$

And the screening functions $S_i(r)$ are defined, for exponential damping (that we use) as:

$$S_0(r) = 1 - \exp\left[-\left(\frac{r}{a}\right)^3\right] + \frac{r}{a} \Gamma\left[\frac{2}{3}, \left(\frac{r}{a}\right)^3\right]$$

$$S_1(r) = 1 - \exp\left[-\left(\frac{r}{a}\right)^3\right]$$

$$S_2(r) = 1 - \left[1 + \left(\frac{r}{a}\right)^3\right] \exp\left[-\left(\frac{r}{a}\right)^3\right]$$

$$S_3(r) = 1 - \left[1 + \left(\frac{r}{a}\right)^3 + \frac{3}{5}\left(\frac{r}{a}\right)^6\right] \exp\left[-\left(\frac{r}{a}\right)^3\right]$$

Each S_k can be obtained recursively:

$$S_k(r) = S_{k-1}(r) - \frac{r}{2k-1} \frac{\partial}{\partial r} S_{k-1}(r)$$

and using r, while we use $a^{1/4} r$

These expressions are from TTM-3 (damping order 3). MB-nrg uses order 4 damping. Thus, we can rewrite them properly. Also, to be consistent, I will use a as the thole damping (a_{CC}, a_{CD}, a_{DD}) and the a in the previous equations will become $A = (\alpha_i \alpha_j)^{1/6}$. Thus, using order 4 damping:

$$S_0(r) = 1 - e^{-a\left(\frac{r}{A}\right)^4} + \frac{a^{1/4} r}{A} \Gamma\left(\frac{3}{4}, a\left(\frac{r}{A}\right)^4\right)$$

$$S_1(r) = 1 - e^{-a\left(\frac{r}{A}\right)^4} \qquad \frac{\partial S_1(r)}{\partial r} = 4a\left(\frac{r}{A}\right)^3 \frac{1}{A} e^{-a\left(\frac{r}{A}\right)^4}$$

$$S_2(r) = S_1(r) - \frac{r}{4-1} 4a\left(\frac{r}{A}\right)^3 \frac{1}{A} e^{-a\left(\frac{r}{A}\right)^4} = S_1(r) - \frac{4a}{3}\left(\frac{r}{A}\right)^4 e^{-a\left(\frac{r}{A}\right)^4} \qquad \frac{\partial S_2}{\partial r} = \frac{4a}{3A}\left(\frac{r}{A}\right)^3 e^{-a\left(\frac{r}{A}\right)^4} \left(4a\left(\frac{r}{A}\right)^4 - 1\right)$$

$$S_3(r) = S_2(r) - \frac{r}{6-1} \left(\frac{4a}{3A}\left(\frac{r}{A}\right)^3 e^{-a\left(\frac{r}{A}\right)^4}\right) \left(4a\left(\frac{r}{A}\right)^4 - 1\right) = S_2(r) - \frac{4a}{15}\left(\frac{r}{A}\right)^4 e^{-a\left(\frac{r}{A}\right)^4} \left(4a\left(\frac{r}{A}\right)^4 - 1\right)$$

As reader can notice, $\hat{T}_{ij}^{\alpha\beta\gamma}$ does not appear in the energy expressions, but is necessary to calculate the forces:

$$F_{i,qq}^\alpha = -\sum_{j \neq i}^{N_q} q_i \hat{T}_{ij}^\alpha q_j \qquad F_{i,q\mu}^\alpha = \sum_{j \neq i}^{N_\mu} \left(q_i \hat{T}_{ij}^{\alpha\beta} \mu_j^\beta - q_j \hat{T}_{ij}^{\alpha\beta} \mu_i^\beta \right) \qquad F_{i,\mu\mu}^\alpha = \sum_{j \neq i}^{N_\mu} \mu_i^\beta \hat{T}_{ij}^{\alpha\beta\gamma} \mu_j^\gamma$$

Electrostatic Interaction Calculation:

1. Fixed Electrostatic Energy and Permanent Electric Field:

$$U_{qq} = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} q_i \hat{T}_{ij} q_j$$ This is the sum of all chg-chg interactions

$$E_i^{q,\alpha} = \sum_{j\neq i}^{N_q} \hat{T}_{ij}^{\alpha} q_j$$ This is the electric field in the direction α (x, y, or z) in site i

2. Obtain the dipoles:

A. Matrix Inversion (C++ reference code, $O(N^3)$)

$\vec{\mu}_i = \hat{\alpha}_i \vec{E}_i$ (1) $\hat{\alpha}_i$ is the polarizability tensor on site i. In our case, all the atoms have isotropic polarizabilities, which means that $\hat{\alpha}_i$ is a scalar.

$$\left.\begin{aligned} E_i^{q,\alpha} &= \sum_{j\neq i}^{N_q} \hat{T}_{ij}^{\alpha} q_j \quad (2) \\ E_i^{\mu,\alpha} &= \sum_{j\neq i}^{N_\mu} \hat{T}_{ij}^{\alpha\beta} \mu_j^{\beta} \quad (3) \end{aligned}\right\}$$ Plugging (2) and (3) in (1), we get:

$$\vec{\mu}_i = \hat{\alpha}_i \left(\vec{E}_i^{q} + \sum_{j\neq i}^{N_\mu} \hat{T}_{ij} \vec{\mu}_j \right) \xRightarrow{\text{Rearranging}} \overleftrightarrow{\mathbb{A}} \, \vec{\mathbb{M}} = \mathbb{E}^q$$, where $$\mathbb{A} = \begin{bmatrix} \hat{\alpha}_1^{-1} & -\hat{T}_{12} & \cdots & -\hat{T}_{1N_\mu} \\ -\hat{T}_{21} & -\hat{\alpha}_2^{-1} & \cdots & -\hat{T}_{2N_\mu} \\ \vdots & \vdots & \ddots & \vdots \\ -\hat{T}_{N_\mu 1} & -\hat{T}_{N_\mu 2} & \cdots & -\hat{\alpha}_{N_\mu}^{-1} \end{bmatrix}$$

One can invert $\mathbb{A}$ and multiply by $\mathbb{E}^q$ to get $\mathbb{M}$: $\mathbb{M} = \mathbb{A}^{-1} \mathbb{E}^q$

B. Iterative Method (DLPOLY, OpenMM. $O(N^2)$)

i) Obtain Permanent Electric Field $E_i^{q,\alpha} = \sum_{j\neq i}^{N_q} \hat{T}_{ij}^{\alpha} q_j \quad \forall\, \alpha, i$

ii) Calculate Dipoles $\vec{\mu}_i = \hat{\alpha}_i \vec{E}_i$

Don't need to recalculate this since it has already been calculated

iii) Recalculate Electric field with the dipoles obtained in ii) $\vec{E}_i^{\alpha} = \vec{E}_i^{\alpha,q} + \vec{E}_i^{\alpha,\mu} \quad \forall\, \alpha, i$

Where $\vec{E}_i^{\alpha,\mu} = \sum_{j\neq i}^{N_\mu} \hat{T}_{ij}^{\alpha\beta} \mu_j^{\beta}$ (Note, sum over β => Einstein notation)

iv) Go to ii) until $\left(|\vec{\mu}_i^{k}| - |\vec{\mu}_i^{k+1}|\right)^2 <$ Tolerance

3. Get the energy contributions

$$U_{el} = U_{qq} + V_{q\mu} + U_{\mu\mu} + U_{dip}^{pol}$$

$$U_{q\mu} = \sum_i \sum_{j>i} \left(\mu_i^{\alpha} \hat{T}_{ij}^{\alpha} q_j - q_i \hat{T}_{ij}^{\alpha} \mu_j^{\alpha} \right)$$

$$U_{\mu\mu} = \sum_i \sum_{i>j} \left(-\mu_i^{\alpha} \hat{T}_{ij}^{\alpha\beta} \mu_j^{\beta} \right)$$

$$U_{dip}^{pol} = \frac{1}{2} \sum_{i=1}^{N_\mu} \vec{\mu}_i \hat{\alpha}_i^{-1} \vec{\mu}_j$$