Multipole Expansion of the Electrostatic Potential

The electrostatic potential in the expression for V_{ext} given above is very general. We will now look at a specific potential, namely one generated by a collection of point charges. A collection of *N* charges at the termini of the vectors $\vec{r}_i$ generates a potential at a point $\vec{R}$.

$$\phi(\vec{R}) = \sum_{i=1}^{N} \frac{q_i}{\left|\vec{R}-\vec{r}_i\right|}$$

where

$$\left|\vec{R}-\vec{r}_i\right| = \sqrt{(R_x - x_i)^2 + (R_y - y_i)^2 + (R_z - z_i)^2}$$

We are interested in the situation where the origin of the coordinate system is in the charge distribution and $\vec{R}$ is external to the charge distribution and much larger than any of the vectors $\vec{r}_i$. Under these circumstances $\vec{r}_i$ is small and an expansion of each term in the series around $\vec{r}_i = 0$ makes sense. Consider a representative term in the summation and expand it around the origin.

$$\frac{1}{\left|\vec{R}-\vec{r}\right|} = f(x,y,z) = f(0,0,0) + \left(\frac{\partial f}{\partial r_\alpha}\right)_0 r_\alpha + \frac{1}{2}\left(\frac{\partial^2 f}{\partial r_\alpha \partial r_\beta}\right)_0 r_\alpha r_\beta + \frac{1}{3!}\left(\frac{\partial^3 f}{\partial r_\alpha \partial r_\beta \partial r_\gamma}\right)_0 r_\alpha r_\beta r_\gamma + \cdots$$

now

$$\frac{\partial f}{\partial x} = \frac{-\dfrac{\partial\left|\vec{R}-\vec{r}\right|}{\partial x}}{\left|\vec{R}-\vec{r}\right|^2}$$

and

$$\frac{\partial\left|\vec{R}-\vec{r}\right|}{\partial x} = \frac{\partial\sqrt{(R_x - x)^2 + (R_y - y)^2 + (R_z - z)^2}}{\partial x} = \frac{-(R_x - x)}{\left|\vec{R}-\vec{r}\right|}$$

so $$\frac{\partial f}{\partial x} = \frac{(R_x - x)}{\left|\vec{R}-\vec{r}\right|^3}$$

and so

$$\left(\frac{\partial f}{\partial x}\right)_0 = \frac{R_x}{R^3}$$

Note that this function is equal to $-\nabla_{R_x}\left(\frac{1}{R}\right)$ where $\nabla_{R_x} = \frac{\partial}{\partial R_x}$. These functions are ubiquitous in the theory of intermolecular forces and are given special names (propagators) and symbols. We define a dipole propagator as

$$T_\alpha = \nabla_\alpha\left(\frac{1}{R}\right) = -\left(\frac{\partial f}{\partial r_\alpha}\right)_0 = -\frac{R_\alpha}{R^3}$$

It's tedious but straight forward to show

$$T_{\alpha\beta} = \nabla_{\alpha\beta}\left(\frac{1}{R}\right) = -\left(\frac{\partial^2 f}{\partial r_\alpha \partial r_\beta}\right)_0 = \frac{(3R_\alpha R_\beta - \delta_{\alpha\beta}R^2)}{R^5}$$

and

$$T_{\alpha\beta\gamma} = \nabla_{\alpha\beta\gamma}\left(\frac{1}{R}\right) = -\left(\frac{\partial^3 f}{\partial r_\alpha \partial r_\beta \partial r_\gamma}\right)_0 = \frac{-3(5R_\alpha R_\beta R_\gamma - R^2(\delta_{\alpha\beta}R_\gamma - \delta_{\alpha\gamma}R_\beta - \delta_{\beta\gamma}R_\alpha)}{R^7}$$

$T_{\alpha\beta}$ & $T_{\alpha\beta\gamma}$ are the quadrupole and octupole propagators. Note that

$$T_{\alpha\beta} = \nabla_\alpha T_\beta \ \ \& \ \ T_{\alpha\beta\gamma} = \nabla_\alpha T_{\beta\gamma},\ etc$$

Our representative term becomes

$$\frac{q}{\left|\vec{R}-\vec{r}\right|} = q\left(\frac{1}{R} - T_\alpha r_\alpha + \frac{1}{2}T_{\alpha\beta}r_\alpha r_\beta - \frac{1}{3!}T_{\alpha\beta\gamma}r_\alpha r_\beta r_\gamma + \cdots\right)$$

and so

$$\phi(R) = \sum_{i=1}^{N} q_i\left(\frac{1}{R} - T_\alpha r_{i\alpha} + \frac{1}{2}T_{\alpha\beta}r_{i\alpha}r_{i\beta} - \frac{1}{3!}T_{\alpha\beta\gamma}r_{i\alpha}r_{i\beta}r_{i\gamma} + \cdots\right)$$

Since the various propagators do not depend on the index *i* we have

$$\phi(\vec{R}) = \frac{Q}{R} - T_\alpha \mu_\alpha + \frac{1}{2}T_{\alpha\beta}A_{\alpha\beta} - \frac{1}{3!}T_{\alpha\beta\gamma}W_{\alpha\beta\gamma} - \cdots$$

Where the various moments, $Q, \mu_{\alpha,} A_{\alpha\beta}$ & $W_{\alpha\beta\gamma}$ have been defined previously. Indeed, since

$$T_{\alpha\alpha} = T_{xx} + T_{yy} + T_{zz} = 0$$

and

$$T_{\alpha\alpha\beta} = T_{\alpha\gamma\alpha} = T_{\lambda\alpha\alpha} = 0$$

We may write the potential in terms of the quadrupole and octupole moments defined previously.

$$\phi(\vec{R}) = \frac{Q}{R} - T_\alpha \mu_\alpha + \frac{1}{3} T_{\alpha\beta} \Theta_{\alpha\beta} - \frac{1}{15} T_{\alpha\beta\gamma} \Omega_{\alpha\beta\gamma} - \cdots$$

Exercise: verify that

$$a.\ T_\alpha T_\alpha = \frac{1}{R^4}$$

$$b.\ T_{\alpha\beta} T_{\alpha\beta} = \frac{6}{R^6}$$