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Electrostatics for Chemists

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I. INTRODUCTION

Chemists rarely study electrostatics after introductory courses have made the subject sufficiently unpalatable that they are eschewed forevermore by many of us. This document revists electrostatics, as needed by chemists, and hopes to provide a friendly and inviting introduction to the subject, in the context of chemical problems, sufficient to allow readers to attain mastery of the subject sufficient for their needs.

II. THE FIELD OF AN ISOLATED POINT CHARGE

We start with the definition of the electric field in the vicinity of a point charge (q) which is located at the position $\vec{r}_i$. We have

$$\vec{E}(\vec{r}) = q_i \frac{\vec{r} - \vec{r}_i}{|\vec{r} - \vec{r}_i|^3}$$

(where $\vec{r} = (x, y, z)$ and $\vec{r}_i$ is the position of a particle setting up the electric field being tested) so that the force felt by a test particle of charge q_{test} located at the point $\vec{x}$ would be

$$\vec{F}(\vec{r}_{test}) = q_{test}\vec{E}(\vec{r}) = q_{test} q_i \frac{\vec{r}_{test} - \vec{r}_i}{|\vec{r}_{test} - \vec{r}_i|^3}$$

If $\vec{r}_i = (0, 0, 0)$ i.e., the particle setting up the electric field is at the origin, then

$$\vec{E}(\vec{r}) = q_i \frac{\vec{r}}{|\vec{r}|^3}$$

There then exists a potential energy function (a function of position of the test particle as well as the point particle which is setting up the field)

$$\nabla\phi = \vec{E}(\vec{r})$$

Since

$$\nabla\left(\frac{1}{r}\right) = -\frac{1}{r^2}\nabla r$$

which equals

$$\nabla\left(\frac{1}{r}\right) = -\frac{1}{r^2}\nabla\sqrt{x^2 + y^2 + z^2}$$

we have, using elementary differentiation

$$-\nabla\left(\frac{1}{r}\right) = \frac{1}{r^2}\frac{\vec{r}}{\sqrt{x^2 + y^2 + z^2}} = \frac{\vec{r}}{r^3} \tag{2.1}$$

we obtain

$$\vec{E}(\vec{x}_{test}) = q_{test}\nabla\frac{1}{r}$$

where r is the distance from the charge to the test point (in essence, this formula changes the origin to the place the original charge at the origin).

III. THE ELECTRIC POTENTIAL (TO FIRST ORDER) OF A DIPOLE

We place our dipole at the origin, aligned with the z-axis, with a plus charge at (0,0,a/2) and the minus charge at (0,0,-a/2), such that the distance of separation is "a". Then we have

$$r_+ = \sqrt{x^2 + y^2 + (z - \frac{a}{2})^2}$$

$$r_- = \sqrt{x^2 + y^2 + (z + \frac{a}{2})^2}$$

Expanding in a Taylor series we have

$$\frac{1}{r_+} = \frac{1}{r} - \frac{z}{r^3}\left(\frac{a}{2}\right) + \cdots$$

$$\frac{1}{r_-} = \frac{1}{r} - \frac{z}{r^3}\left(\frac{-a}{2}\right) + \cdots$$

from which we conclude that, to first order,

$$\phi = \frac{q}{r_+} + \frac{-q}{r_-} = q\frac{za}{r^3} \equiv \frac{\vec{\mu}\cdot\vec{r}}{r^3} \tag{3.1}$$

where r is the distance from the origin (the center of the dipole) to the test particle located at (x,y,z). Since $z \times a = \vec{\mu}\cdot\vec{r}$, the last part of this equation is a generalization in case the dipole is not oriented as shown (above).
Higher order terms in the Taylor expansion lead to multipole terms, e.g., quadrupoles and octopoles, as examples.

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IV. THE ELECTRIC FIELD OF A DIPOLE

From the definition,

$$\vec{E} = -\nabla\phi$$

where, for a point dipole, i.e., one whose $q \times a$ remains fixed at a pre-fixed value while the charge separation goes to zero (and the charges rise/fall to maintain the constancy of the dipole moment),

$$\lim_{a\to 0, q_+\to\infty} q \times a = |\vec{\mu}| = constant$$

becomes

$$\vec{E} = -\nabla\left(\frac{\vec{\mu}\cdot\vec{r}}{r^3}\right)$$

(Equation 3.1) which is the result we just had. Performing the calculus we have

$$\vec{E} = -\left(\vec{\mu}\cdot\vec{r}\right)\nabla\left(\frac{1}{r^3}\right) - \frac{1}{r^3}\nabla\left(\vec{\mu}\cdot\vec{r}\right)$$

which gives

$$\vec{E} = \frac{3\vec{\mu}\cdot\vec{r}}{r^5}\vec{r} - \frac{1}{r^3}\left(\vec{\mu}\right)$$

Assuming there are two particle, #1 and #2, each with its own charge and point dipole. We have acting on particle 2 by virtue of the presence of particle 1,

$$\vec{E}_{1\to 2} = \frac{3\vec{\mu_1}\cdot\vec{r}_{1\to 2}}{r_{12}^5}\vec{r}_{1\to 2} - \frac{1}{r_{12}^3}\vec{\mu_1}$$

due to particle 1 acting on 2, and

$$\vec{E}_{2\to 1} = \frac{3\vec{\mu_2}\cdot\vec{r}_{2\to 1}}{r_{12}^5}\vec{r}_{2\to 1} - \frac{1}{r_{12}^3}\vec{\mu_2}$$

due to particle 2 acting on 1, asuming each is a point dipole! This is only the dipole part of the total electric field, so adding the Coulombic term (2.1) we have

$$\vec{E}(\vec{r}_2) = \vec{E}_{1\to 2} = \frac{3\vec{\mu}_1\cdot\vec{r}_{1\to 2}}{r_{12}^5}\vec{r}_{1\to 2} - \frac{\vec{\mu}_1}{r_{12}^3} + \frac{q_1\vec{r}_{1\to 2}}{r_{12}^3} \quad (4.1)$$

due to particle 1 acting on 2, and

$$\vec{E}(\vec{r}_1) = \vec{E}_{2\to 1} = \frac{3\vec{\mu}_2\cdot\vec{r}_{2\to 1}}{r_{12}^5}\vec{r}_{2\to 1} - \frac{\vec{\mu}_2}{r_{12}^3} + \frac{q_2\vec{r}_{2\to 1}}{r_{12}^3} \quad (4.2)$$

V. VARIABLE INDUCED DIPOLES

For the situation in which the dipole moments are themselves proportional to the applied electric field (first order polarization) we have

$$\vec{\mu}_1 = \alpha_1\vec{E}(\vec{r}_1)$$

and

$$\vec{\mu}_2 = \alpha_2\vec{E}(\vec{r}_2)$$

so, substituting into Equations 4.2 and 4.1 we obtain

$$\vec{\mu}_2 = \left(\frac{3\vec{\mu_1}\cdot\vec{r}_{1\to 2}}{r_{12}^5}\vec{r}_{1\to 2} - \frac{1}{r_{12}^3}\vec{\mu_1} + \frac{q_1\vec{r}_{1\to 2}}{r_{12}^3}\right)\alpha_2 \quad (5.1)$$

due to particle 1 acting on 2, and

$$\vec{\mu}_1 = \left(\frac{3\vec{\mu_2}\cdot\vec{r}_{2\to 1}}{r_{12}^5}\vec{r}_{2\to 1} - \frac{1}{r_{12}^3}\vec{\mu_2} + \frac{q_2\vec{r}_{1\to 2}}{r_{12}^3}\right)\alpha_1 \quad (5.2)$$

A. Dyadic Notation

It is normal to attempt to combine the first two terms (above) (using Equation 5.2) into a single term. First, we note

$$\vec{\mu}_2\cdot\vec{r}_{2\to 1} = \mu_x^{(2)}(x_1 - x_2) + \mu_y^{(2)}(y_1 - y_2) + \mu_z^{(2)}(z_1 - z_2)$$

and further, we note that

$$\left(\vec{\mu}_2\cdot\vec{r}_{2\to 1}\right)\vec{r}_{2\to 1} = \left(\vec{\mu}_2\cdot\vec{r}_{1\to 2}\right)\vec{r}_{1\to 2} \quad (5.3)$$

(where we notice the double sign change induced by the permutation of 1 into 2 and *vice versa*. Expanding the r.h.s. of the above (Equation 5.3), we have

$$\begin{aligned}
&\left(\mu_x^{(2)}(x_2 - x_1) + \mu_y^{(2)}(y_2 - y_1) + \mu_z^{(2)}(z_2 - z_1)\right)(x_2 - x_1)\hat{\imath} \\
&\left(\mu_x^{(2)}(x_2 - x_1) + \mu_y^{(2)}(y_2 - y_1) + \mu_z^{(2)}(z_2 - z_1)\right)(y_2 - y_1)\hat{\jmath} \\
&\left(\mu_x^{(2)}(x_2 - x_1) + \mu_y^{(2)}(y_2 - y_1) + \mu_z^{(2)}(z_2 - z_1)\right)(z_2 - z_1)\hat{k}
\end{aligned} \quad (5.4)$$

which allows a rearrangement to

$$\begin{pmatrix} (x_2-x_1)^2 & (y_2-y_1)(x_2-x_1) & (z_2-z_1)(x_2-x_1) \\ (x_2-x_1)(y_2-y_1) & (y_2-y_1)^2 & (y_2-y_1)(x_2-x_1) \\ (x_2-x_1)(y_2-y_1) & (y_2-y_1)(z_2-z_1) & (z_2-z_1)^2 \end{pmatrix} \begin{pmatrix} \mu_x^{(2)} \\ \mu_y^{(2)} \\ \mu_z^{(2)} \end{pmatrix} \tag{5.5}$$

Notice that the operator is now operating on a dipole vector, not a spatial vector.
This allows us to re-write (see Equation 4.2) as:

$$\vec{E}(\vec{r}_1) = \vec{E}_{2\to1} = \frac{3\vec{\mu}_2\cdot\vec{r}_{2\to1}}{r_{12}^5}\vec{r}_{2\to1} - \frac{\vec{\mu}_2}{r_{12}^3} + \frac{q_2\vec{r}_{2\to1}}{r_{12}^3} =$$
$$3\begin{pmatrix} (x_2-x_1)^2 & (y_2-y_1)(x_2-x_1) & (z_2-z_1)(x_2-x_1) \\ (x_2-x_1)(y_2-y_1) & (y_2-y_1)^2 & (y_2-y_1)(x_2-x_1) \\ (x_2-x_1)(y_2-y_1) & (y_2-y_1)(z_2-z_1) & (z_2-z_1)^2 \end{pmatrix} \begin{pmatrix} \mu_x^{(2)} \\ \mu_y^{(2)} \\ \mu_z^{(2)} \end{pmatrix} - \frac{1}{r_{12}^3}\begin{pmatrix} \mu_x^{(2)} \\ \mu_y^{(2)} \\ \mu_z^{(2)} \end{pmatrix}$$
$$+\frac{q_2}{r_{12}^3}\begin{pmatrix} x_1-x_2 \\ y_1-y_2 \\ z_1-z_2 \end{pmatrix} \tag{5.6}$$

Combining the first two terms (which only became possible because of the complicated rearrangement we just did), we obtain

$$\vec{E}(\vec{r}_1) = \vec{E}_{2\to1} = \begin{pmatrix} \left(\frac{3(x_2-x_1)^2}{r_{12}^5} - \frac{1}{r_{12}^3}\right) & \frac{3(y_2-y_1)(x_2-x_1)}{r_{12}^5} & \frac{3(z_2-z_1)(x_2-x_1)}{r_{12}^5} \\ \frac{3(x_2-x_1)(y_2-y_1)}{r_{12}^5} & \left(\frac{3(y_2-y_1)^2}{r_{12}^5} - \frac{1}{r_{12}^3}\right) & \frac{3(z_2-z_1)(y_2-y_1)}{r_{12}^5} \\ \frac{3(x_2-x_1)(y_2-y_1)}{r_{12}^5} & \frac{3(y_2-y_1)(z_2-z_1)}{r_{12}^5} & \left(\frac{3(z_2-z_1)^2}{r_{12}^5} - \frac{1}{r_{12}^3}\right) \end{pmatrix} \begin{pmatrix} \mu_x^{(2)} \\ \mu_y^{(2)} \\ \mu_z^{(2)} \end{pmatrix}$$
$$-\frac{q_2}{r_{12}^3}\begin{pmatrix} x_1-x_2 \\ y_1-y_2 \\ z_1-z_2 \end{pmatrix} \tag{5.7}$$

with the symmetric form

$$\vec{E}(\vec{r}_2) = \vec{E}_{1\to2} = \begin{pmatrix} \left(\frac{3(x_2-x_1)^2}{r_{12}^5} - \frac{1}{r_{12}^3}\right) & \frac{3(y_2-y_1)(x_2-x_1)}{r_{12}^5} & \frac{3(z_2-z_1)(x_2-x_1)}{r_{12}^5} \\ \frac{3(x_2-x_1)(y_2-y_1)}{r_{12}^5} & \left(\frac{3(y_2-y_1)^2}{r_{12}^5} - \frac{1}{r_{12}^3}\right) & \frac{3(z_2-z_1)(y_2-y_1)}{r_{12}^5} \\ \frac{3(x_2-x_1)(y_2-y_1)}{r_{12}^5} & \frac{3(y_2-y_1)(z_2-z_1)}{r_{12}^5} & \left(\frac{3(z_2-z_1)^2}{r_{12}^5} - \frac{1}{r_{12}^3}\right) \end{pmatrix} \begin{pmatrix} \mu_x^{(1)} \\ \mu_y^{(1)} \\ \mu_z^{(1)} \end{pmatrix}$$
$$-\frac{q_1}{r_{12}^3}\begin{pmatrix} x_2-x_1 \\ y_2-y_1 \\ z_2-z_1 \end{pmatrix} \tag{5.8}$$

We can now define a special tensor like quantity:

$$\mathcal{T}_{i,j} = \left(\frac{3\vec{r}_{i,j}\odot\vec{r}_{i,j}}{r_{i,j}^2} - 1\right)$$

where

$$\left(\frac{3\vec{r}_{i,j}\odot\vec{r}_{i,j}}{r_{i,j}^2} - 1\right) \equiv \begin{pmatrix} \left(\frac{3(x_j-x_i)^2}{r_{ij}^5} - \frac{1}{r_{ij}^3}\right) & \frac{3(y_j-y_i)(x_j-x_i)}{r_{ij}^5} & \frac{3(z_j-z_i)(x_j-x_i)}{r_{ij}^5} \\ \frac{3(x_j-x_i)(y_j-y_i)}{r_{ij}^5} & \left(\frac{3(y_j-y_i)^2}{r_{ij}^5} - \frac{1}{r_{ij}^3}\right) & \frac{3(z_j-z_i)(y_j-y_i)}{r_{ij}^5} \\ \frac{3(x_j-x_i)(y_j-y_i)}{r_{ij}^5} & \frac{3(y_j-y_i)(z_j-z_i)}{r_{ij}^5} & \left(\frac{3(z_j-z_i)^2}{r_{ij}^5} - \frac{1}{r_{ij}^3}\right) \end{pmatrix} \tag{5.9}$$

which allows us to re-write

$$\vec{E}(\vec{r}_1) = \vec{E}_{2\to1} = \frac{\mathcal{T}_{1,2}\odot\vec{\mu}^{(2)}}{r_{1,2}^3} - \left(\frac{q_2}{r_{12}^3}\right)\vec{r}_{12} \tag{5.10}$$

and

$$\vec{E}(\vec{r}_2) = \vec{E}_{1\to 2} = \frac{\mathcal{T}_{2,1} \odot \vec{\mu}^{(1)}}{r_{1,2}^3} - \left(\frac{q_1}{r_{12}^3}\right)\vec{r}_{21} \tag{5.11}$$

Notice that the magnitudes are the same, just the vectors change upon considering each of a pair or point dipoles.

VI. ELECTRIC POLARIZATION INDUCING DIPOLES

$$\vec{\mu}_1 = \alpha_1 \times \left\{ \begin{pmatrix} \left(\frac{3(x_2-x_1)^2}{r_{12}^5} - \frac{1}{r_{12}^3}\right) & \frac{3(y_2-y_1)(x_2-x_1)}{r_{12}^5} & \frac{3(z_2-z_1)(x_2-x_1)}{r_{12}^5} \\ \frac{3(x_2-x_1)(y_2-y_1)}{r_{12}^5} & \left(\frac{3(y_2-y_1)^2}{r_{12}^5} - \frac{1}{r_{12}^3}\right) & \frac{3(z_2-z_1)(y_2-y_1)}{r_{12}^5} \\ \frac{3(x_2-x_1)(y_2-y_1)}{r_{12}^5} & \frac{3(y_2-y_1)(z_2-z_1)}{r_{12}^5} & \left(\frac{3(z_2-z_1)^2}{r_{12}^5} - \frac{1}{r_{12}^3}\right) \end{pmatrix} \begin{pmatrix} \mu_x^{(2)} \\ \mu_y^{(2)} \\ \mu_z^{(2)} \end{pmatrix} - q_2 \frac{\vec{r}_{12}}{r_{12}^3} \right\} \tag{6.1}$$

or

$$\vec{\mu}_1 = \alpha_1 \vec{E}_{2\to 1} = \alpha_1 \left(\frac{\mathcal{T}_{1,2} \odot \vec{\mu}^{(2)}}{r_{1,2}^3} - \left(\frac{q_2}{r_{12}^3}\right)\vec{r}_{12} \right) \tag{6.2}$$

and

$$\vec{\mu}_2 = \alpha_2 \times \left\{ \begin{pmatrix} \left(\frac{3(x_2-x_1)^2}{r_{12}^5} - \frac{1}{r_{12}^3}\right) & \frac{3(y_2-y_1)(x_2-x_1)}{r_{12}^5} & \frac{3(z_2-z_1)(x_2-x_1)}{r_{12}^5} \\ \frac{3(x_2-x_1)(y_2-y_1)}{r_{12}^5} & \left(\frac{3(y_2-y_1)^2}{r_{12}^5} - \frac{1}{r_{12}^3}\right) & \frac{3(z_2-z_1)(y_2-y_1)}{r_{12}^5} \\ \frac{3(x_2-x_1)(y_2-y_1)}{r_{12}^5} & \frac{3(y_2-y_1)(z_2-z_1)}{r_{12}^5} & \left(\frac{3(z_2-z_1)^2}{r_{12}^5} - \frac{1}{r_{12}^3}\right) \end{pmatrix} \begin{pmatrix} \mu_x^{(1)} \\ \mu_y^{(1)} \\ \mu_z^{(1)} \end{pmatrix} + q_1 \frac{\vec{r}_{12}}{r_{12}^3} \right\} \tag{6.3}$$

or

$$\vec{\mu}_2 = \alpha_2 \vec{E}_{1\to 2} = \alpha_2 \left(\frac{\mathcal{T}_{2,1} \odot \vec{\mu}^{(1)}}{r_{1,2}^3} - \left(\frac{q_1}{r_{12}^3}\right)\vec{r}_{21} \right) \tag{6.4}$$

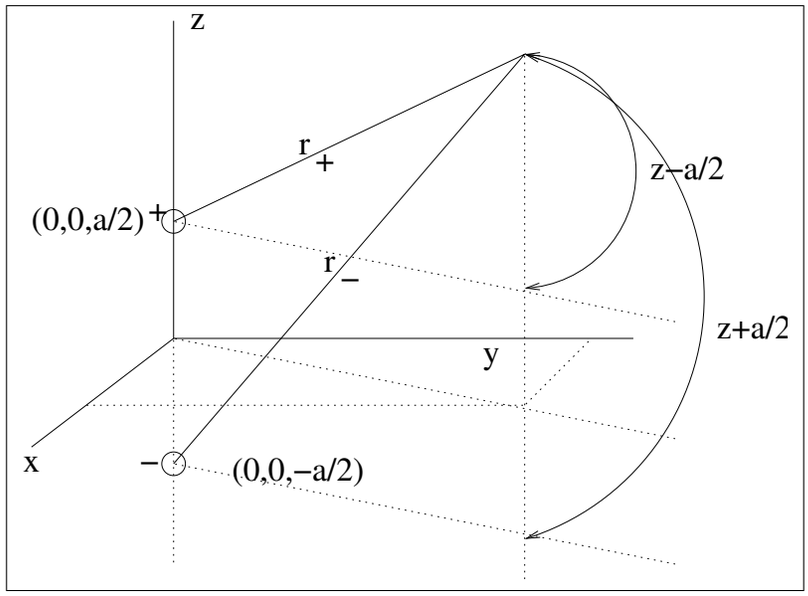

FIG. 1: A Dipole, located at the origin and oriented along the z-axis. q_+ is at (0,0,a/2) and q_- is at 0,0,-a/2).