Multipole moments

Dipole moment

The second moment $\vec{\mu}$ is more commonly called the dipole moment, of the charge distribution and is a vector

$$\vec{\mu} = \mu_x \hat{x} + \mu_y \hat{y} + \mu_z \hat{z}$$

where the α component is given by

$$\mu_\alpha = \sum_{i=1}^{N} q_i r_{i\alpha}$$

where α can be $x, y,$ *or* z and $\vec{r}_i$ is the coordinate of the i^{th} particle relative to some origin. The dimensions of the dipole moment are charge-length and the most common unit for the dipole moment in Chemistry is the Debye, (D), and 1D =10^{-18} esu-cm. This is a cgs unit and is still used even though the official system of units in now the SI system. An easy way to convert between the systems is to note that in the cgs system the dipole moment of a proton and an electron separated by 1Angstrom is 4.8029 10^{-18} esu cm or 4.8029D. In the SI system the same dipole moment is (1.60217733 10^{-19}C)(10^{-10}M) or 1.60218 10^{-29} CM so 1D is equal to (1.60218/4.8029) 10^{-29} CM or 3.33586 10^{-30} CM/D. In theoretical work the dipole moment is often reported in atomic units and by the same reasoning 4.8029D is equal to (1electron charge)(1/0.5291772)a_0 or 1.889726 au so 1D is equivalent to 0.39346 au. Conversely 1 atomic unit of dipole moment is equal to 2.54159D.

Exercise

Calculate the dipole moment in D and au for the charge distributions given below. The distances are given in Angstroms and e is the proton charge.

charge	*x*	*y*	*z*
e	*0*	*1*	*1*
e	*0*	*-1*	*1*
-2e	*0*	*0*	*0*

charge	*x*	*y*	*z*
e	*0*	*1*	*1*
e	*0*	*-1*	*2*
-2e	*0*	*0*	*0*

How is the dipole moment affected if we shift the origin of the coordinate system to the point $\vec{R}$? The particles have not moved but are now at the terminus of the vector $\vec{r}_i - \vec{R}$ so relative to the new origin μ_α becomes

$$\mu_\alpha(\vec{R}) = \sum_{i=1}^{N} q_i (r_{i\alpha} - R_\alpha) = \sum_{i=1}^{N} q_i r_{i\alpha} - R_\alpha \sum_{i=1}^{N} q_i$$

or

$$\mu_\alpha(\vec{R}) = \mu_\alpha(0) - R_\alpha Q$$

Where *Q* is the total charge of the distribution and if the charge distribution is neutral, *Q* is zero and the dipole moment is invariant to a change of origin. Note that when we move to the new origin we simply translate the coordinate system. We keep the x, y, z axis in the two systems parallel. Suppose we don't move the origin but rotate the coordinate axis keeping them orthogonal. Lets call the original coordinate axis x, y, z and the rotated system x', y', z'. The vector $\vec{\mu}$ is the two systems is

$$\vec{\mu} = \mu_x \hat{x} + \mu_y \hat{y} + \mu_z \hat{z} = \mu_{x'} \hat{x}' + \mu_{y'} \hat{y}' + \mu_{z'} \hat{z}'$$

Taking the dot product of both sides with $\hat{x}'$, recognizing that the unit vectors in the primed system are all orthogonal we obtain

$$\mu_{x'} = \mu_x \hat{x} \bullet \hat{x}' + \mu_y \hat{y} \bullet \hat{x}' + \mu_z \hat{z} \bullet \hat{x}'$$

The dot products are equal to the cosines of the angle between the various axis which we call $a_{xx'}, a_{yx'}$ & $a_{zx'}$ and so

$$\mu_{x'} = \mu_x a_{xx'} + \mu_y a_{yx'} + \mu_z a_{zx'}$$

With a similar expression for $\mu_{y'}$ & $\mu_{z'}$. These relationships are often written in matrix form as

$$\begin{pmatrix} \mu_{x'} \\ \mu_{y'} \\ \mu_{z'} \end{pmatrix} = \begin{pmatrix} a_{xx'} & a_{yx'} & a_{zx'} \\ a_{xy'} & a_{yy'} & a_{zy'} \\ a_{xz'} & a_{yz'} & a_{zz'} \end{pmatrix} \begin{pmatrix} \mu_x \\ \mu_y \\ \mu_z \end{pmatrix}$$

Using the Einstein summation convention we can write the relationship between the components of the dipole moment in the rotated and un-rotated systems as

$$\mu_{\alpha'} = \mu_\beta a_{\beta\alpha'}$$

and although the individual components of the dipole moment change when the coordinate axis are rotated, its magnitude doesn't so we must have

$$\mu_{\alpha'}\mu_{\alpha'} = \mu_\alpha \mu_\alpha$$

or

$$\mu_{\alpha'}\mu_{\alpha'} = \mu_\alpha a_{\alpha\alpha'}\mu_\beta a_{\beta\alpha'} = \mu_\alpha \mu_\beta a_{\alpha\alpha'}a_{\beta\alpha'} = \mu_\alpha \mu_\alpha$$

which requires

$$a_{\alpha\alpha'}a_{\beta\alpha'} = \delta_{\alpha\beta}$$

where $\delta_{\alpha\beta}$ is the Kronecker delta which is 1 if $\alpha = \beta$ and zero otherwise.

Exercise

Consider the charge distribution

charge	*x*	*y*	*z*
e	*0*	*1*	*1*
e	*0*	*-1*	*1*
-2e	*0*	*0*	*0*

rotate the coordinate axis about x by 30 degrees. Compare the components and magnitude of the dipole moment in the two coordinate frames.

Exercise

a. Calculate the interaction energy (in J and eV) between a proton at the origin and the charge distribution given below (distances are in Angstroms and e is the proton charge).

charge	*x*	*y*	*z*
e	*5*	*2*	*1*
-e	*6*	*2*	*1*

b. Calculate the interaction energy with the proton due to the dipole moment of the distribution. Express your answer in J and eV.

c. Comment on the difference between the results of parts a and b.

Quadrupole and Higher Moments

There are two common definitions for the quadrupole moment of a charge distribution. The first and least common in Chemistry equates the quadrupole moment tensor with the second moment tensor $A_{\alpha\beta}$ defined above. The second definition and the one we will use almost exclusively defines it as

$$\Theta_{\alpha\beta} = \frac{1}{2}\sum_{i=1}^{N} q_i(3\xi_{i\alpha}\xi_{i\beta} - \delta_{\alpha\beta}\xi_i^2) = \frac{3}{2}A_{\alpha\beta} - \frac{\delta_{\alpha\beta}}{2}\sum_{i=1}^{N}\xi_i^2$$

Note that

$$-\frac{1}{3}\Theta_{\alpha\beta}F_{\alpha\beta} = -\frac{1}{2}A_{\alpha\beta}F_{\alpha\beta} + \frac{1}{6}\delta_{\alpha\beta}F_{\alpha\beta}\sum_{i=1}^{N}\xi_i^2$$

but

$$\delta_{\alpha\beta}F_{\alpha\beta} = F_{\alpha\alpha} = \nabla_\alpha F_\alpha = \nabla_\alpha\nabla_\beta\phi = \nabla^2\phi = 0$$

by Laplace's equation. So the energy of the second moment in a field gradient can be written in terms of the quadrupole moment tensor as

$$-\frac{1}{2}A_{\alpha\beta}F_{\alpha\beta} = -\frac{1}{3}\Theta_{\alpha\beta}F_{\alpha\beta}$$

$\Theta_{\alpha\beta}$ is often called the Buckingham definition of the quadrupole moment. There are 9 elements for the quadrupole moment tensor but not all are unique. Permuting the indices doesn't change its value so

$$\Theta_{\alpha\beta} = \Theta_{\beta\alpha}$$

Additionally the tensor is traceless, so

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

So knowing any two of the diagonal elements will determine the third. In the most general case where none of the element are related by the symmetry of the charge distribution, we will have 3 unique non-diagonal elements, Θ_{xy}, Θ_{xz} & Θ_{yz} and any two diagonal elements for a total of 5. Symmetry often reduces this number significantly. If we have a linear charge distribution along the z axis, all non-diagonal elements are zero, and $\Theta_{xx} = \Theta_{yy} = -\frac{1}{2}\Theta_{zz}$ and only one element is unique.

Exercise

Express the quadrupole moment tensor of the following charge distributions in terms of the charges Q and bond lengths R.

$C_{\infty V}$ array along the z axis

Atom	*charge*	*x*	*y*	*z*
1	*q*	*0*	*0*	*-R*
2	*-2q*	*0*	*0*	*0*
3	*q*	*0*	*0*	*R*

Planar D_{3h} in the xy plane

Atom	*charge*	*x*	*y*	*z*
1	*q*	*R cos30*	*R sin30*	*0*
2	*q*	*-R cos30*	*R sin30*	*0*
3	*q*	*0*	*-R*	*0*
4	*-3q*	*0*	*0*	*0*

Tetrahedral array

atom	*charge*	*x*	*y*	*z*
1	*q*	$R/\sqrt{3}$	$-R/\sqrt{3}$	$R/\sqrt{3}$
2	*q*	$-R/\sqrt{3}$	$R/\sqrt{3}$	$R/\sqrt{3}$
3	*q*	$-R/\sqrt{3}$	$-R/\sqrt{3}$	$-R/\sqrt{3}$
4	*q*	$R/\sqrt{3}$	$R/\sqrt{3}$	$-R/\sqrt{3}$
5	*-4q*	*0*	*0*	*0*

Exercise

Calculate numerical values for the quadrupole tensors of the above charge distributions assuming that $q = 0.1e$ *and R= 1Angstrom. Report your results in the SI and atomic unit systems.*

In a similar fashion we can replace the third moment $W_{\alpha\beta\gamma}$ with an octupole moment tensor defined as

$$\Omega_{\alpha\beta\chi} = -\frac{1}{2}\sum_{i=1}^{N} q_i (5\xi_{i\alpha}\xi_{i\beta}\xi_{i\gamma} - \xi_i^2(\xi_{i\alpha}\delta_{\beta\gamma} + \xi_{i\beta}\delta_{\alpha\gamma} + \xi_{i\gamma}\delta_{\alpha\beta}))$$

because one can show, with the use of Laplace's equation,

$$-\frac{1}{3!}W_{\alpha\beta\gamma}F_{\alpha\beta\gamma} = -\frac{1}{15}\Omega_{\alpha\beta\gamma}F_{\alpha\beta\gamma}$$

There are 27 elements (3^3) of this tensor but again not all are unique. As with the quadrupole moment, permuting any two indices doesn't change the value of the element. For example,

$$\Omega_{xxy} = \Omega_{xyx} = \Omega_{yxx}$$

additionally the tensor is traceless, for example

$$\Omega_{\alpha\alpha y} = \Omega_{xxy} + \Omega_{yyy} + \Omega_{zzy} = 0$$

So knowing any two of the elements $\Omega_{\alpha\alpha\beta}$ determines the third. In the most general case where none of the elements are related by the symmetry of the charge distribution, one could have a maximum of 7 unique elements.

The working expression for the potential energy of a charge distribution in an electrostatic potential is then

$$V_{ext} = Q\phi(\vec{R}) - \mu_\alpha F_\alpha - \frac{1}{3}\Theta_{\alpha\beta}F_{\alpha\beta} - \frac{1}{3\bullet 5}\Omega_{\alpha\beta\gamma}F_{\alpha\beta\gamma} - \frac{1}{3\bullet 5\bullet 7}\Phi_{\alpha\beta\gamma\delta}F_{\alpha\beta\gamma\delta} -$$

where for completeness we include the hexadecapole moment tensor, $\Phi_{\alpha\beta\gamma\delta}$

The general formula for a multipole moment of order *L* is

$$M^L_{\alpha\beta\cdots\gamma} = \frac{(-1)^L Q}{L!}\sum_{i=1}^{N}\xi_i^{2L+1}\left(\frac{\partial^L}{\partial\xi_{i\alpha}\,\partial\xi_{i\beta}\cdots\partial\xi_{i\gamma}}\left(\frac{1}{\xi_i}\right)\right)$$

where

$$\xi_i = \sqrt{\xi_{ix}^2 + \xi_{iy}^2 + \xi_{iz}^2}$$

& $M^0 = Q$, $M^1_\alpha = \mu_\alpha$, $M^2_{\alpha\beta} = \Theta_{\alpha\beta}$, $M^3_{\alpha\beta\gamma} = \Omega_{\alpha\beta\gamma}$, etc.