A DEEPER LOOK 8 The electric dipole–dipole interaction

An important problem in physical chemistry is the calculation of the potential energy of interaction between two point electric dipoles with moments $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$, separated by a vector $\boldsymbol{r}$. The starting point is an expression from classical electromagnetic theory for the potential energy of $\boldsymbol{\mu}_2$ in the electric field $\mathcal{E}_1$ generated by $\boldsymbol{\mu}_1$:

$$V = -\mathcal{E}_1 \cdot \boldsymbol{\mu}_2 \qquad (1)$$

In three dimensions, the strength of the electric field (a scalar quantity) can be expressed in terms of ϕ, the *Coulomb potential* due to the distribution of charges in the system, as

$$\mathcal{E}_1 = -\nabla\phi \qquad (2)$$

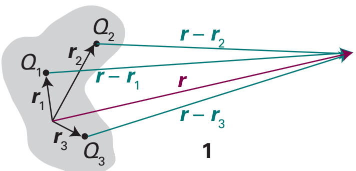
where the result of the operation ∇ on a function $f(x,y,z)$ is a vector with x, y, and z components calculated by forming $\partial f/\partial x$, $\partial f/\partial y$, and $\partial f/\partial z$, respectively:

$$\nabla f = \left(\frac{\partial f}{\partial x}\right)_{y,z}\hat{\boldsymbol{i}} + \left(\frac{\partial f}{\partial y}\right)_{z,x}\hat{\boldsymbol{j}} + \left(\frac{\partial f}{\partial z}\right)_{x,y}\hat{\boldsymbol{k}} \qquad (3)$$

The goal is then to write an expression for $\mathcal{E}_1$, and then take the dot (scalar) product of $\mathcal{E}_1$ with $\boldsymbol{\mu}_2$.

Step 1 *Write an expression for the Coulomb potential*

To calculate $\mathcal{E}_1$, consider a distribution of point charges Q_i located at x_i, y_i, and z_i from the origin (1). Let $\boldsymbol{r}$ be a vector pointing from the origin (0,0,0) to the location of the point of interest (x,y,z), and $\boldsymbol{r}_i$ a vector pointing from the origin to the locations of the charges Q_i, with coordinates (x_i,y_i,z_i). It follows that the magnitude of $\boldsymbol{r}$ is $r = (x^2 + y^2 + z^2)^{1/2}$, that of $\boldsymbol{r}_i$ is $r_i = (x_i^2 + y_i^2 + z_i^2)^{1/2}$, and that the magnitude of the resultant $\boldsymbol{r} - \boldsymbol{r}_i$ is $r_{\text{res}} = \{(x-x_i)^2 + (y-y_i)^2 + (z-z_i)^2\}^{1/2}$. The Coulomb potential ϕ due to this distribution at a point with coordinates x, y, and z is:



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$$\phi = \sum_i \frac{Q_i}{4\pi\varepsilon_0}\frac{1}{\{(x-x_i)^2+(y-y_i)^2+(z-z_i)^2\}^{1/2}} \qquad (4)$$

Step 2 *Make approximations*

If all the charges are close to the origin (in the sense that $r_i \ll r$ and $r_{\text{res}} \approx r$), then a Taylor expansion (*The chemist's toolkit* 12 in Topic 5B) can be used to write

$$\phi = \sum_i \frac{Q_i}{4\pi\varepsilon_0}\left\{\frac{1}{r} + \left(\frac{\partial\{(x-x_i)^2+(y-y_i)^2+(z-z_i)^2\}^{-1/2}}{\partial x_i}\right)_{x_i=0} x_i + \cdots\right\} \qquad (5a)$$

where the ellipses include the terms arising from derivatives with respect to y_i and z_i and higher derivatives. Because of the approximations being made, the derivative in blue evaluates to

$$\left(\frac{\partial\left\{(x-x_i)^2+(y-y_i)^2+(z-z_i)^2\right\}^{-1/2}}{\partial x_i}\right)_{x_i=0} = \left(\frac{x-x_i}{\left\{(x-x_i)^2+(y-y_i)^2+(z-z_i)^2\right\}^{3/2}}\right)_{x_i=0} = \frac{x}{r_{\text{res}}^3} \approx \frac{x}{r^3}$$

It follows that

$$\phi = \sum_i \frac{Q_i}{4\pi\varepsilon_0}\left\{\frac{1}{r} + \frac{x x_i}{r^3} + \cdots\right\} \qquad (5b)$$

If the charge distribution is electrically neutral, the first term disappears because $\sum_i Q_i = 0$. Next note that, $\sum_i Q_i x_i = \mu_x$ and likewise for the y- and z-components. That is,

$$\phi = \frac{1}{4\pi\varepsilon_0 r^3}(\mu_x x + \mu_y y + \mu_z z) + \cdots = \frac{1}{4\pi\varepsilon_0 r^3}\boldsymbol{\mu}_1 \cdot \boldsymbol{r} + \cdots \qquad (5c)$$

The higher-order terms correspond to the higher multipoles of the charge distribution, and will be considered no further here.

Step 3 *Write an expression for the electric field strength*

It follows from eqns 2 and 5 that the electric field strength is

$$\mathcal{E}_1 = -\frac{1}{4\pi\varepsilon_0}\nabla\frac{\boldsymbol{\mu}_1 \cdot \boldsymbol{r}}{r^3} \qquad (6a)$$

To evaluate the derivative in this expression, first note that $\nabla(fg) = f\nabla g + g\nabla f$, so

$$\nabla\frac{\boldsymbol{\mu}_1 \cdot \boldsymbol{r}}{r^3} = \frac{1}{r^3}\nabla(\boldsymbol{\mu}_1 \cdot \boldsymbol{r}) + (\boldsymbol{\mu}_1 \cdot \boldsymbol{r})\nabla\frac{1}{r^3}$$

It follows that:

- The result of the operation $\nabla(\boldsymbol{\mu}_1 \cdot \boldsymbol{r}) = \nabla(\mu_x x + \mu_y y + \mu_z z)$ is a vector with components

$$\frac{\partial}{\partial x}\mu_x x = \mu_x \qquad \frac{\partial}{\partial y}\mu_y y = \mu_y \qquad \frac{\partial}{\partial z}\mu_z z = \mu_z$$

These are the components of the vector $\boldsymbol{\mu}_1$, so $\nabla(\boldsymbol{\mu}_1 \cdot \boldsymbol{r}) = \boldsymbol{\mu}_1$.

- The result of the operation $\nabla(1/r^3)=\nabla\{(x^2+y^2+z^2)^{-3/2}\}$ is a vector with components

$$\frac{\partial}{\partial x}\frac{1}{(x^2+y^2+z^2)^{3/2}}=-\frac{3x}{(x^2+y^2+z^2)^{5/2}}=-\frac{3}{r^5}x$$

$$\frac{\partial}{\partial y}\frac{1}{(x^2+y^2+z^2)^{3/2}}=-\frac{3y}{(x^2+y^2+z^2)^{5/2}}=-\frac{3}{r^5}y$$

$$\frac{\partial}{\partial z}\frac{1}{(x^2+y^2+z^2)^{3/2}}=-\frac{3z}{(x^2+y^2+z^2)^{5/2}}=-\frac{3}{r^5}z$$

That is,

$$\nabla\frac{1}{r^3}=\frac{3}{r^5}(x\hat{\boldsymbol{i}}+y\hat{\boldsymbol{j}}+z\hat{\boldsymbol{k}})=-\frac{3}{r^5}\boldsymbol{r}$$

The electric field strength is therefore

$$\mathcal{E}_1=-\frac{\boldsymbol{\mu}_1}{4\pi\varepsilon_0 r^3}+3\frac{(\boldsymbol{\mu}_1\cdot\boldsymbol{r})\boldsymbol{r}}{4\pi\varepsilon_0 r^5} \qquad (6b)$$

Step 4 *Write an expression for the potential energy of interaction*

It follows from eqns 1 and 6b that

$$V=-\left\{-\frac{\boldsymbol{\mu}_1}{4\pi\varepsilon_0 r^3}+3\frac{(\boldsymbol{\mu}_1\cdot\boldsymbol{r})\boldsymbol{r}}{4\pi\varepsilon_0 r^5}\right\}\cdot\boldsymbol{\mu}_2$$

and

$$V=\frac{\boldsymbol{\mu}_1\cdot\boldsymbol{\mu}_2}{4\pi\varepsilon_0 r^3}-3\frac{(\boldsymbol{\mu}_1\cdot\boldsymbol{r})(\boldsymbol{r}\cdot\boldsymbol{\mu}_2)}{4\pi\varepsilon_0 r^5}$$

$$=\frac{1}{4\pi\varepsilon_0 r^3}\left\{\boldsymbol{\mu}_1\cdot\boldsymbol{\mu}_2-3\frac{(\boldsymbol{\mu}_1\cdot\boldsymbol{r})(\boldsymbol{r}\cdot\boldsymbol{\mu}_2)}{r^2}\right\} \qquad (7)$$

A similar expression, with magnetic dipole moments in place of electric dipole moments, applies to magnetic interactions (see *The chemist's toolkit* 27 in Topic 12B).