

Review of Electrostatics

The Coulombic force on charge j due to charge i is:

$$\vec{F}_j = \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}^2} \vec{r}_{ij}$$

The Coulombic force is additive. The combined force is a superposition. The force on charge k due to a number of charges with the index j is:

$$\vec{F}_k = \frac{1}{4\pi\epsilon_0} \sum_{j \neq k} \frac{q_j q_k}{r_{jk}^2} \vec{r}_{jk}$$

The constant ϵ_0 is the permittivity of vacuum. In MKS units the value is $\epsilon_0 = 8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$. In the cgs-esu unit system the permittivity of free space is $1/4\pi$ and the constant $1/4\pi\epsilon_0$ does not appear in the Coulomb force.

Electric Field

The electric field is the force per unit charge. The most precise statement is that it is the force per unit charge in the limit that the charge is infinitesimally small:

$$\vec{E}_j = \frac{\partial \vec{F}_j}{\partial q}$$

When applied to the Coulomb force the electric field becomes:

$$\vec{E}_k = \frac{1}{4\pi\epsilon_0} \sum_{j \neq k} q_j \frac{\vec{r}_{jk}}{r_{jk}^2}$$

Electrostatic Potential

The electric field is the negative gradient of the scalar potential:

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

The potential at a distance r from a charge is:

$$\phi = - \frac{q}{4\pi\epsilon_0 r}$$

The electric field represents the force per unit charge.
The potential is the work per unit charge.

$$W_{12} = \phi(q_2 - q_1)$$

In MKS units the potential has units of V where $1 \text{ V} = 1 \text{ J/C}$.

Potential and Field due to a Dipole

The potential due to a dipole is:

$$\phi(r) = \frac{\vec{\mu} \cdot \vec{r}}{4\pi\epsilon_0 r^3}$$

The assumption in this equation is that the distance between the charge and dipole, r , is large relative to the separation of charges in the dipole, d , $r \gg d$.

The electric field due to a dipole is:

$$\vec{E} = \frac{1}{4\pi\epsilon_0} \left(\frac{3(\vec{\mu} \cdot \vec{r})\vec{r}}{r^5} - \frac{\vec{\mu}}{r^3} \right)$$

Using the expression $W = -\vec{\mu} \cdot \vec{E}$ we can calculate the interaction energy of two dipoles.

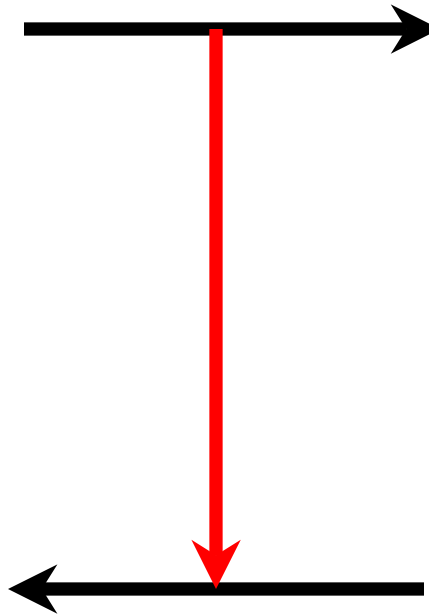
$$W = \frac{1}{4\pi\epsilon_0} \left(\frac{\vec{\mu}_1 \cdot \vec{\mu}_2}{r^3} - \frac{3(\vec{\mu}_1 \cdot \vec{r})(\vec{\mu}_2 \cdot \vec{r})}{r^5} \right)$$

Example: Effect of Dipole Orientation

Consider two dipoles, which have the orientations below that we can call aligned



and head-to-tail



Aligned: $\mu_1 \cdot \mu_2 = \mu^2$, $\mu_1 \cdot r = \mu r$, $\mu_2 \cdot r = \mu r$, $W = -2\mu^2/4\pi\epsilon_0 r^3$

Head-to-tail: $\mu_1 \cdot \mu_2 = -\mu^2$, $\mu_1 \cdot r = 0$, $\mu_2 \cdot r = 0$, $W = -\mu^2/4\pi\epsilon_0 r^3$

Electric moments

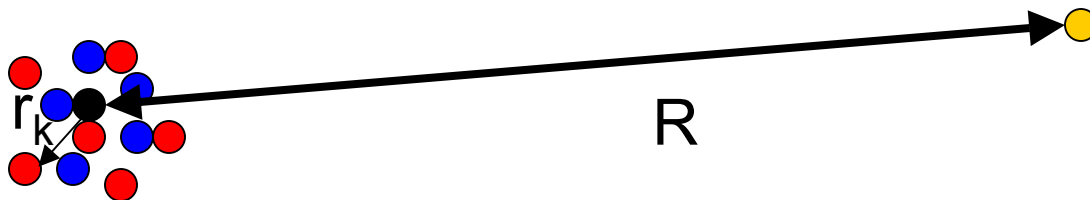
The potential due to discrete charge distribution is:

$$\phi(\mathbf{R}) = \frac{1}{4\pi\epsilon_0} \sum_k \frac{q_k}{|\mathbf{R} - \mathbf{r}_k|}$$

If the distance R of the test charge is large relative to the distances between the charges then the expansion:

$$\frac{1}{|\mathbf{R} - \mathbf{r}_k|} = \frac{1}{R} + r_k \cdot \nabla \left(\frac{1}{R} \right) + \frac{1}{2} r_k \cdot r_k : \nabla \nabla \left(\frac{1}{R} \right) + \dots$$

can be made



Electric moments

The potential is then given by:

$$4\pi\epsilon_0\phi(\mathbf{R}) = \frac{q}{R} + \boldsymbol{\mu} \cdot \nabla \left(\frac{1}{R} \right) + \frac{1}{2} \Theta : \nabla \nabla \left(\frac{1}{R} \right) + \dots$$

This is the multipole expansion. The terms are the charge (also called the monopole), q , the dipole, $\boldsymbol{\mu}$, the quadrupole, Θ , and higher order terms.

$$q = \sum_i q_i = \int \rho(\vec{r}) d\vec{r}$$

$$\boldsymbol{\mu} = \sum_i q_i \vec{r}_i = \int \rho(\vec{r}) \vec{r} d\vec{r}$$

$$\Theta = \sum_j \sum_i q_i \vec{r}_i \vec{r}_j = \int \rho(\vec{r}) \vec{r} \vec{r} d\vec{r}$$

q is a scalar,

$\boldsymbol{\mu}$ is a vector (a first rank tensor)

Θ is a matrix (a second rank tensor)

Interaction of electric moments with the electric field

The interaction of a collection of charges subjected to an electric field is given by:

$$W = q\phi - \boldsymbol{\mu} \cdot \mathbf{E} + \frac{1}{2} \Theta : \nabla \mathbf{E} + \dots$$

The picture is that of a charge interacting with the potential, the dipole interacting with a field, the quadrupole interacting with the field gradient etc.

An electric field can exert a force:

$$F = \sum_i q_i E(r_i)$$

or a torque:

$$T = \sum_i r_i \times q_i E(r_i)$$

on a collection of charges.

Polarizability

In the presence of an externally applied electric field the dipole moment of the molecule can also be expressed as an expansion in terms of moments:

$$\boldsymbol{\mu} = \boldsymbol{\mu}_0 - \boldsymbol{\alpha} \cdot \mathbf{E} + \frac{1}{2} \boldsymbol{\beta} : \mathbf{E}\mathbf{E} + \dots$$

The leading term in this expansion is the permanent dipole moment, $\boldsymbol{\mu}_0$. The polarizability is a tensor whose components can be described as follows:

$$\alpha_{xy} = \left(\frac{\partial \mu_x}{\partial E_y} \right)_0$$

Where the 0 subscript refers to the fact that the derivative is evaluated at zero field. The $\boldsymbol{\beta}$ tensor is called the hyperpolarizability and is third ranked tensor.

Polarizability as second rank tensor

The dipole moment components each can depend on as many as three different polarizability components as described by the matrix:

$$\begin{pmatrix} \mu_x \\ \mu_y \\ \mu_z \end{pmatrix} = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix}$$

If a molecule has a center of symmetry (e.g. CCl_4) then the polarizability is a scalar (i.e. the induced dipole moment is always in the direction of the applied field). However, for non-centrosymmetric molecules components can be induced in other directions. The directions are often determined by the directions of chemical bonds, which may not be aligned with the field. This is the significance of the tensor.

Properties of the polarizability tensor

Like the quadrupole moment, the polarizability can be made diagonal in the principle axes of the molecule.

In the laboratory frame of reference the polarizability depends on the orientation of the molecule.

The average polarizability is independent of orientation. It is given by the Trace, which is written $\text{Tr } \alpha$.

$$\text{Tr } \alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

The polarizability increases with the number of electrons in the molecule or with the volume of the charge distribution.

Classically, for a molecule of radius a , $\alpha = 4\pi\epsilon_0 a^3$.

Lorentz (classical) polarizability

The Lorentz model is given here. An electron in one dimension is subject to an electric field that results in a displacement from the center of charge. For a displacement in the x direction (this is the polarization of the electric field, i.e. the electric vector of radiation) the induced moment is given by:

$$\mu_{ind} = -ex = \alpha E$$

The restoring force is:

$$F = -kx = -m\omega_0^2 x$$

The force is balanced by the force due to the applied electric field $F = eE$. The balance of forces is:

$$-m\omega_0^2 x = eE$$

Lorentz polarizability

Thus x is:

$$x = -\frac{eE}{m\omega_0^2}$$

and the dipole moment is:

$$\mu_{ind} = \frac{e^2}{m\omega_0^2}E$$

The classical Lorentz polarizability is:

$$\alpha = \frac{e^2}{m\omega_0^2}$$

The expression can be generalized by letting there be N electrons on a molecule. Each electron has an intrinsic harmonic oscillator frequency. The fraction of the electrons in each of the j modes is f_j . The polarizability for all of the electrons is:

$$\alpha = \frac{e^2}{m} \sum_j \frac{f_j}{\omega_j^2}$$

Frequency dependence of polarizability

The quantity f_j is the oscillator strength. The above treatment is for a static field. In the case where $E(t)$ is a sinusoidal field the equation resembles that of a driven harmonic oscillator.

$$F = m \frac{d^2 x}{dt^2} = -eE(t) - m\omega_0^2 x(t) - \Gamma \frac{dx}{dt}$$

In addition to the electric force and the harmonic restoring force we have added a frictional force. The time dependent electric field must have the form $E(t) = E_{0x} \exp[i(ky - \omega t)]$.

Therefore, we try a solution of the form $x(t) = x_0 \exp[i(ky - \omega t)]$.

$$\frac{dx}{dt} = -i\omega x_0 \exp(i(ky - \omega t))$$

$$\frac{d^2 x}{dt^2} = -\omega^2 x_0 \exp(i(ky - \omega t))$$

Frequency dependence of polarizability

The equation becomes:

$$-\omega^2 x(t) = -\frac{e}{m} E(t) - \omega_0^2 x(t) + \frac{i\omega\Gamma}{m} x(t)$$

Collecting terms in $x(t)$ solving for $x(t)$ we have:

$$x(t) = \frac{-\frac{e}{m} E(t)}{\omega_0^2 - \omega^2 - \frac{i\omega\Gamma}{m}}$$

$$\alpha(\omega) = \frac{e^2}{m} \sum_j \frac{f_j}{\omega_j^2 - \omega^2 - \frac{i\omega\Gamma}{m}}$$

We can also define the polarizability $\alpha = -ex(t)/E(t)$ so the polarizability has real and imaginary parts. These are obtained by multiplying both numerator and denominator by $\omega_j^2 - \omega^2 + i\omega\Gamma/m$.

Frequency dependence of polarizability

The complex polarizability is:

$$\begin{aligned}\alpha(\omega) &= \frac{e^2}{m} \sum_j \frac{f_j}{\omega_j^2 - \omega^2 - \frac{i\omega\Gamma}{m}} \frac{\omega_j^2 - \omega^2 + \frac{i\omega\Gamma}{m}}{\omega_j^2 - \omega^2 + \frac{i\omega\Gamma}{m}} \\ &= \frac{e^2}{m} \sum_j f_j \left(\frac{(\omega_j^2 - \omega^2)}{(\omega_j^2 - \omega^2)^2 + \left(\frac{\omega\Gamma}{m}\right)^2} + i \frac{\frac{\omega\Gamma}{m}}{(\omega_j^2 - \omega^2)^2 + \left(\frac{\omega\Gamma}{m}\right)^2} \right)\end{aligned}$$

Clearly the polarizability consists of real and imaginary parts. We can write it as

$$\alpha(\omega) = \alpha'(\omega) + i\alpha''(\omega)$$

Kramer's Kronig Relations

The real and imaginary parts are related to one another through the Kramers-Kronig relations

$$\alpha'(\omega) = \frac{2}{\pi} \int_0^{\infty} \frac{s\alpha''(s)ds}{s^2 - \omega^2}$$

$$\alpha''(\omega) = \frac{-2\omega}{\pi} \int_0^{\infty} \frac{\alpha'(s)ds}{s^2 - \omega^2}$$

Oscillator Strength

The oscillator strength is a classical formalism. The oscillator strength f_{ij} is proportional to the intensity of a transition $i \rightarrow j$. It is a number less than one and in fact the sum of all of the oscillator strengths in the molecule equals one. Thus,

$$\sum_j f_{ij} = 1$$

Comparison of the quantum treatment with the Lorentz formulation gives

$$f_{0j} = \frac{2m(\mu_{0j})^2 \omega_{j0}}{3e^2 \hbar}$$

The factor of 1/3 arises because only one polarization of electromagnetic radiation is considered here.