Chapter 4
Electric Multipole

4.1 Point Dipole and Quadrupole

4.1.1 The point dipole

A point dipole consists of two opposite point charges, $+q$ and $-q$, separated by a distance d, as shown in **Figure 4.1**. The electric dipole moment $\vec{p}$ is a vector and defined as,

$$\vec{p} = q\vec{d}, \tag{4.1}$$

where $\vec{d}$ is a location vector pointing from the negative charge to positive charge, with a magnitude $|\vec{d}| = d$. The dipole moment encapsulates both the strength and direction of the dipole, providing insight into its electric field characteristics.

Next, we consider the electrostatic potential and electric field generated at a point P located at position $\vec{r}$ due to the dipole, which is centered at $\vec{r}'$. The potential φ_d produced at point P is the result of the superposition of the potentials from both charges,

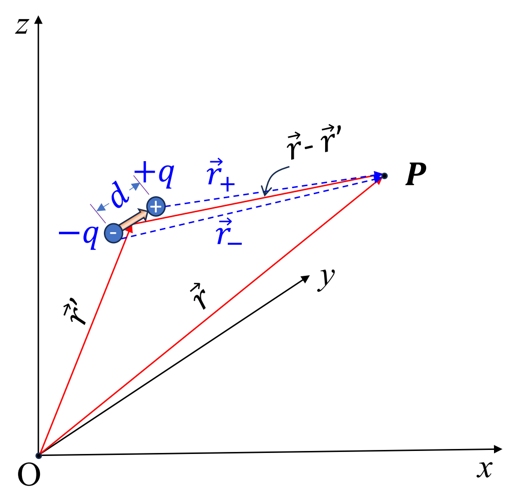


Fig. 4.1 A point dipole and the field and potential generated at *P*.

$$\varphi_d(\vec{r}) = \varphi_+(\vec{r}_+) + \varphi_-(\vec{r}_-) = \frac{q}{4\pi\varepsilon_0}\left(\frac{1}{r_+} - \frac{1}{r_-}\right), \tag{4.2}$$

where $\vec{r}_+$ and $\vec{r}_-$ are the location vectors from the positive charge and negative charge to P, as shown in **Figure 4.1**. Let $\vec{R} = \vec{r} - \vec{r}'$, then $\vec{r}_+ = \vec{R} - \frac{\vec{d}}{2}$ and $\vec{r}_- = \vec{R} + \frac{\vec{d}}{2}$. Thus, we can rewrite the potential as

$$\varphi_d(\vec{r}) = \frac{q}{4\pi\varepsilon_0}\left(\frac{1}{\left|\vec{R}-\frac{\vec{d}}{2}\right|} - \frac{1}{\left|\vec{R}+\frac{\vec{d}}{2}\right|}\right) = \frac{q}{4\pi\varepsilon_0}\left(\frac{1}{\sqrt{R^2+\frac{d^2}{4}-\vec{d}\cdot\vec{R}}} - \frac{1}{\sqrt{R^2+\frac{d^2}{4}+\vec{d}\cdot\vec{R}}}\right). \tag{4.3}$$

For cases where $R \gg d$, we can simplify this expression. By applying the binomial approximation, we have

$$\varphi_d(\vec{r}) \approx \frac{q}{4\pi\varepsilon_0 R}\left(\frac{1}{\sqrt{1-\frac{\vec{d}\cdot\vec{R}}{R^2}}} - \frac{1}{\sqrt{1+\frac{\vec{d}\cdot\vec{R}}{R^2}}}\right). \tag{4.4}$$

Using a Taylor expansion for small quantities, we arrive at,

$$\varphi_d(\vec{r}) \approx \frac{q}{4\pi\varepsilon_0}\frac{\vec{d}\cdot\vec{R}}{R^3} = \frac{\vec{p}\cdot\vec{R}}{4\pi\varepsilon_0\left|\vec{R}\right|^3} = \frac{\vec{p}\cdot(\vec{r}-\vec{r}\prime)}{4\pi\varepsilon_0|\vec{r}-\vec{r}\prime|^3}. \tag{4.5}$$

This expression shows that the potential due to a point dipole diminishes with the square of the distance, which is characteristic of dipolar fields. To find the electric field $\vec{E}_d$ produced at point P, we take the negative gradient of the potential,

$$\vec{E}_d = -\nabla\varphi_d(\vec{r}) = -\frac{1}{4\pi\varepsilon_0}\nabla\left[\vec{p}\cdot\frac{(\vec{r}-\vec{r}\prime)}{|\vec{r}-\vec{r}\prime|^3}\right]. \tag{4.6}$$

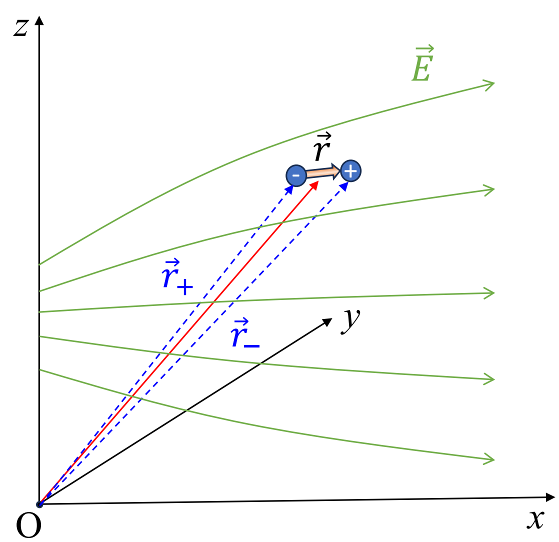


Fig. 4.2 A point dipole in an external electric field $\vec{E}(\vec{r})$.

Applying the identity $\nabla(\vec{A}\cdot\vec{B}) = (\vec{A}\cdot\nabla)\vec{B} + (\vec{B}\cdot\nabla)\vec{A} + \vec{A}\times(\nabla\times\vec{B}) + \vec{B}\times(\nabla\times\vec{A})$ and the following relationships $\nabla\times\vec{p} = 0$, $\nabla\times\frac{(\vec{r}-\vec{r}\prime)}{|\vec{r}-\vec{r}\prime|^3} = 0$, and $\left[\frac{(\vec{r}-\vec{r}\prime)}{|\vec{r}-\vec{r}\prime|^3}\cdot\nabla\right]\vec{p} = 0$, we obtain the expression for the electric field outside the dipole,

$$\vec{E}_d = \frac{1}{4\pi\varepsilon_0}\left[\frac{3\hat{R}(\hat{R}\cdot\vec{p})-\vec{p}}{|\vec{R}|^3}\right]. \tag{4.7}$$

However, it is important to note that at the location $\vec{r} = \vec{r}'$, which is the center of the dipole, the expression for the electric field $\vec{E}_d$ exhibits a singularity. To account for this, we can modify the expression to incorporate the distribution of the two point charges that constitute the dipole,

$$\vec{E}_d = \frac{1}{4\pi\varepsilon_0}\left[\frac{3\hat{R}(\hat{R}\cdot\vec{p})-\vec{p}}{|\vec{R}|^3} - \frac{4\pi}{3}\vec{p}\delta(\vec{R})\right]. \tag{4.8}$$

This adjustment accounts for the infinite electric field at the dipole's center by introducing a delta function that represents the localized charge distribution.

Taylor expansion

For an arbitrary function $f(x)$, the value of the function at $x+\epsilon$, with $\epsilon \sim 0$, can be expressed as

$$f(x+\epsilon) = f(x) + \epsilon\frac{df(x)}{dx} + \frac{1}{2!}\epsilon^2\frac{d^2f(x)}{dx^2} + \frac{1}{3!}\epsilon^3\frac{d^3f(x)}{dx^3} + \cdots$$
$$= \left[1 + \epsilon\frac{d}{dx} + \frac{1}{2!}\epsilon^2\frac{d^2}{dx^2} + \frac{1}{3!}\epsilon^3\frac{d^3}{dx^3} + \cdots\right]f(x) = \exp\left(\epsilon\frac{d}{dx}\right)f(x).$$

For a function with a 3D position vector $f(\vec{r})$, the Taylor expansion can be written as,

$$f(\vec{r}+\vec{\epsilon}) = f(x+\epsilon_x, y+\epsilon_y, z+\epsilon_z)$$
$$= f(x,y,z) + \left(\epsilon_x\frac{\partial f}{\partial x} + \epsilon_y\frac{\partial f}{\partial y} + \epsilon_z\frac{\partial f}{\partial z}\right)$$
$$+\frac{1}{2!}\left(\epsilon_x^2\frac{\partial^2 f}{\partial x^2} + \epsilon_y^2\frac{\partial^2 f}{\partial y^2} + \epsilon_z^2\frac{\partial^2 f}{\partial z^2} + \epsilon_x\epsilon_y\frac{\partial^2 f}{\partial x\partial y} + \epsilon_y\epsilon_z\frac{\partial^2 f}{\partial y\partial z} + \epsilon_z\epsilon_x\frac{\partial^2 f}{\partial z\partial x}\right) + \cdots$$
$$= f(\vec{r}) + \vec{\epsilon}\cdot\nabla f(\vec{r}) + \frac{1}{2!}(\vec{\epsilon}\cdot\nabla)^2 f(\vec{r}) + \frac{1}{3!}(\vec{\epsilon}\cdot\nabla)^3 f(\vec{r}) + \cdots$$

Therefore,

$$f(\vec{r}+\vec{\epsilon}) = \exp(\vec{\epsilon}\cdot\nabla)f(\vec{r}).$$

Force and Torque on a Dipole

The force acting on the dipole when it is placed in an external electric field can be determined by calculating the electrostatic energy U_d of the dipole, as shown in **Figure 4.2**,

$$U_d = U_+ + U_- = q\varphi(\vec{r}_+) - q\varphi(\vec{r}_-) = q\varphi\left(\vec{r} + \frac{\vec{d}}{2}\right) - q\varphi\left(\vec{r} - \frac{\vec{d}}{2}\right). \quad (4.9)$$

In general, $r \gg d$, we can use a Taylor expansion to approximate the potentials at the two positions,

$$\begin{cases} \varphi\left(\vec{r} + \frac{\vec{d}}{2}\right) \approx \varphi(\vec{r}) + \frac{\vec{d}}{2} \cdot \nabla\varphi(\vec{r}) \\ \varphi\left(\vec{r} - \frac{\vec{d}}{2}\right) \approx \varphi(\vec{r}) - \frac{\vec{d}}{2} \cdot \nabla\varphi(\vec{r}) \end{cases}. \quad (4.10)$$

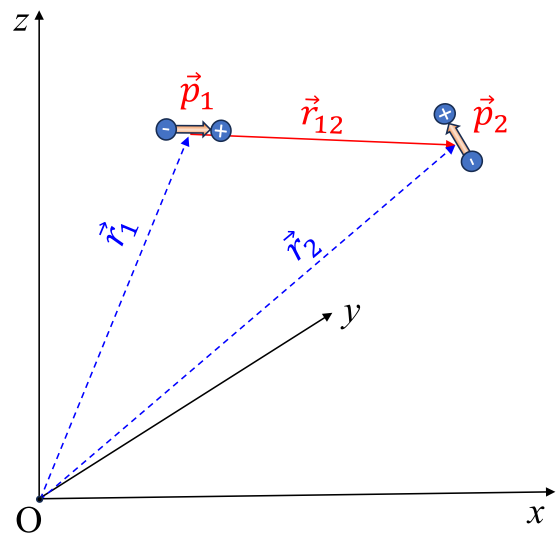


Fig. 4.3 The interaction between two-point dipoles.

Substituting these approximations back into **Equation 4.9**, we find,

$$U_d = q\vec{d} \cdot \nabla\varphi(\vec{r}) = -\vec{p} \cdot \vec{E}(\vec{r}). \quad (4.11)$$

This relationship indicates that the potential energy of the dipole in the electric field depends on the alignment of the dipole moment $\vec{p}$ with the electric field $\vec{E}(\vec{r})$.

The force $\vec{F}_d$ acting on the dipole can be written as,

$$\vec{F}_d = -\nabla U_d = \nabla\left[\vec{p} \cdot \vec{E}(\vec{r})\right] = (\vec{p} \cdot \nabla)\vec{E}(\vec{r}). \quad (4.12)$$

This equation shows that the force on the dipole is proportional to the gradient of the electric field, indicating that the dipole experiences a net force in non-uniform electric fields.

Similar, the torque $\vec{N}$ acting on the dipole can be expressed as,

$$\vec{N} = \vec{p} \times \vec{E}. \tag{4.13}$$

Interaction Between Two Point Dipoles

To investigate the interaction of two point dipoles, as shown in **Figure 4.3**, the dipole $\vec{p}_1$ generates an electric potential $\varphi_1(\vec{r}_2)$ and an electric field $\vec{E}_1(\vec{r}_2)$ at the position of dipole $\vec{p}_2$ according to **Equations 4.5** and **4.7**,

$$\varphi_1(\vec{r}_2) = \frac{\vec{p}_1 \cdot \vec{r}_{21}}{4\pi\varepsilon_0 |\vec{r}_{21}|^3}, \tag{4.14}$$

$$\vec{E}_1(\vec{r}_2) = \frac{1}{4\pi\varepsilon_0}\left[\frac{3\hat{r}_{21}(\hat{r}_{21} \cdot \vec{p}_1) - \vec{p}_1}{|\vec{r}_{21}|^3}\right], \tag{4.15}$$

where $\vec{r}_{21} = \vec{r}_2 - \vec{r}_1$. According to **Equation 4.11**, the interaction energy U_{12} between the two dipoles can be written as,

$$U_{12} = -\vec{p}_2 \cdot \vec{E}_1 = \frac{1}{4\pi\varepsilon_0}\left[\frac{\vec{p}_1 \cdot \vec{p}_2 - 3(\hat{r}_{21} \cdot \vec{p}_2)(\hat{r}_{21} \cdot \vec{p}_1)}{|\vec{r}_{21}|^3}\right], \tag{4.16}$$

Finally, the electrostatic force $\vec{F}_{12}$ acting on dipole $\vec{p}_2$ can be written as,

$$\vec{F}_{12} = (\vec{p}_2 \cdot \nabla_2)\vec{E}_1(\vec{r}_2), \tag{4.17}$$

where ∇_2 is the gradient operator with respect to $\vec{r}_2$.

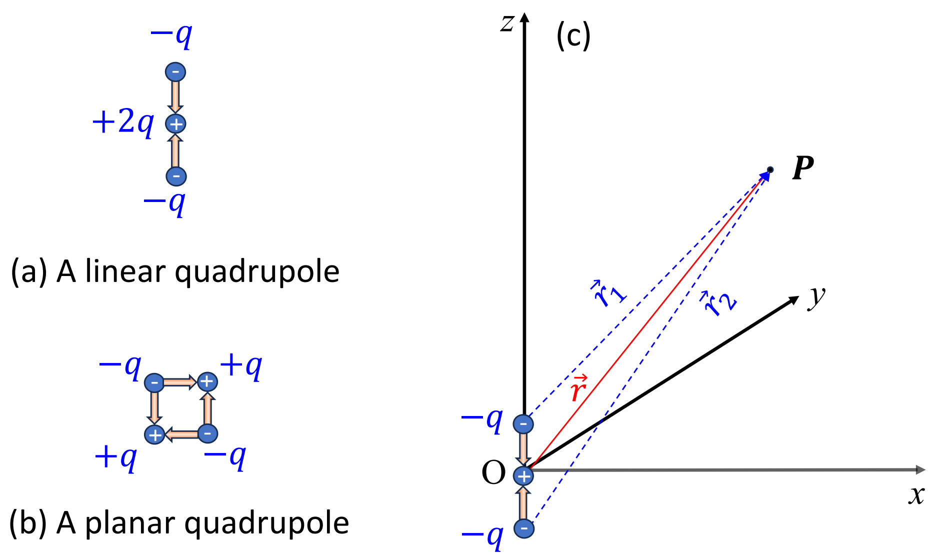


Fig. 4.4 (a) A linear and (b) planar quadrupole configuration. (c) The interaction between two point dipoles.

4.1.2 The point quadrupole

An electric quadrupole consists of a spatial distribution of two dipoles, typically arranged in such a way that their combined effects yield a net charge and dipole moment of zero. This arrangement can take on two configurations, as illustrated in **Figure 4.4**. In the linear quadrupole configuration (shown in **Figure 4.4a**), the two dipoles are aligned along the same straight line. In contrast, the nonlinear quadrupole configuration (depicted in **Figure 4.4b**) has the dipoles oriented along different axes.

The quadrupole moment is represented by a second-rank tensor $\boldsymbol{Q}$,

$$\boldsymbol{Q} = \begin{pmatrix} Q_{xx} & Q_{xy} & Q_{xz} \\ Q_{yx} & Q_{yy} & Q_{yz} \\ Q_{zx} & Q_{zy} & Q_{zz} \end{pmatrix}, \tag{4.18}$$

with its components defined as follows

$$\begin{cases} Q_{xx} = \sum_{j=1}^{N} q_i x_i^2 \\ Q_{xy} = \sum_{j=1}^{N} q_i x_i y_i \end{cases}. \tag{4.19}$$

For a quadrupole formed from four point charges, as shown in **Figure 4.4**, we set $N = 4$. For example, in the case of a linear quadrupole shown in **Figure 4.4c**, we can specify the positions of the charges,

$$\begin{cases} q_1 = -q,\ \vec{r}_1 = (0,0,a) \\ q_2 = 2q,\ \vec{r}_2 = (0,0,0) \\ q_3 = -q,\ \vec{r}_3 = (0,0,-a) \end{cases}.$$

Calculating the components of the quadrupole moment yields,

$$Q_{xx} = Q_{yy} = 0,$$

$$Q_{zz} = -qa^2 + 0 - qa^2 = -2qa^2,$$

$$Q_{xy} = Q_{yx} = Q_{yz} = Q_{zy} = Qq_{xz} = Q_{zx} = 0.$$

Thus, the quadrupole moment tensor becomes,

$$\boldsymbol{Q} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -2qa^2 \end{pmatrix}, \tag{4.20}$$

The electrostatic potential $\varphi_q(\vec{r})$ generated by a linear quadrupole shown in **Figure 4.4c** can be calculated as,

$$\varphi_q(\vec{r}) = \frac{-q}{4\pi\varepsilon_0 r_1} + \frac{2q}{4\pi\varepsilon_0 r} - \frac{-q}{4\pi\varepsilon_0 r_2} = \frac{2q}{4\pi\varepsilon_0 r} - \frac{q}{4\pi\varepsilon_0}\left(\frac{1}{|\vec{r}-\vec{a}|} + \frac{1}{|\vec{r}+\vec{a}|}\right). \tag{4.21}$$

Assume that $a \ll r$ and apply a Taylor expansion, we fin

$$\varphi_q(\vec{r}) = \frac{2q}{4\pi\varepsilon_0 r} - \frac{q}{4\pi\varepsilon_0}\left(\frac{1}{\sqrt{r^2+a^2-2\vec{a}\cdot\vec{r}}} + \frac{1}{\sqrt{r^2+a^2+2\vec{a}\cdot\vec{r}}}\right)$$

$$= \frac{q}{8\pi\varepsilon_0 r}\frac{a^2-2\vec{a}\cdot\vec{r}}{r^2} + \frac{q}{8\pi\varepsilon_0 r}\frac{a^2+2\vec{a}\cdot\vec{r}}{r^2} - \frac{q}{4\pi\varepsilon_0 r}\frac{3}{8}\left[\left(\frac{a^2-2\vec{a}\cdot\vec{r}}{r^2}\right)^2 + \left(\frac{a^2+2\vec{a}\cdot\vec{r}}{r^2}\right)^2\right]$$

$$= \frac{qa^2}{4\pi\varepsilon_0 r^3} - \frac{3q(\vec{a}\cdot\vec{r})^2}{4\pi\varepsilon_0 r^5} = \frac{Q_{zz}}{4\pi\varepsilon_0 r^3}(3\cos^2\theta - 1), \quad (4.22)$$

where θ is the angle between the vector $\vec{a}$ (aligned along the z-axis) and the position vector $\vec{r}$.

For a planar quadrupole with the following arrangement,

$$\begin{cases} q_1 = -q,\ \vec{r}_1 = (-a, 0, a) \\ q_2 = +q,\ \vec{r}_2 = (a, 0, a) \\ q_3 = -q,\ \vec{r}_3 = (a, 0, -a) \\ q_4 = +q,\ \vec{r}_4 = (-a, 0, -a) \end{cases}.$$

The components of the quadrupole moment can be calculated as,

$$Q_{xx} = Q_{yy} = Q_{zz} = 0,$$

$$Q_{xy} = Q_{yx} = Q_{zy} = Q_{yz} = 0,$$

$$Q_{xz} = Q_{zx} = 4qa^2.$$

Thus, the quadrupole moment tensor for this configuration is given by,

$$\boldsymbol{Q} = \begin{pmatrix} 0 & 0 & 4qa^2 \\ 0 & 0 & 0 \\ 4qa^2 & 0 & 0 \end{pmatrix}. \quad (4.23)$$

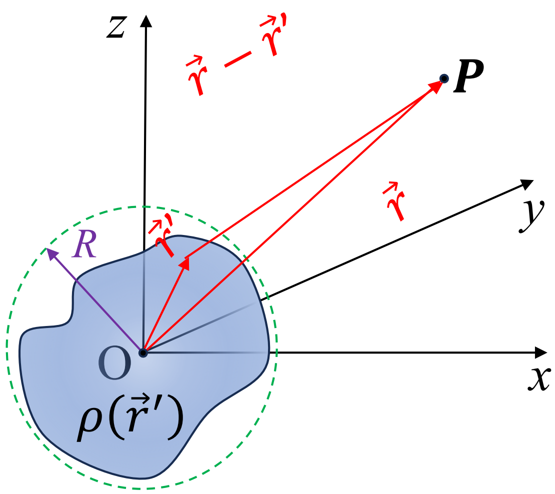


Fig. 4.5 A charged object with a finite volume.

4.2 Electric Multipole Expansion

4.2.1 Multipole expansion in Cartesian coordinates

According to **Equation 3.13**, for a bulk charge distribution V_1 shown in **Figure 4.5**, the potential $\varphi(\vec{r})$ can be expressed as,

$$\varphi(\vec{r}) = \frac{1}{4\pi\varepsilon_0}\iiint_{V_1} \frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} dV'. \tag{3.13}$$

Here we position the center of the charge distribution at the origin of the coordinate system and assume that the charge distribution is confined within a finite volume defined by the maximum radius R (i.e., $r' \leq R$). When considering a location P at position $\vec{r}$ that is far away from the charged object, i.e., $r \gg R$, we can expand the expression $\frac{1}{|\vec{r}-\vec{r}'|}$ in **Equation 3.13** in terms of $\vec{r}'$,

$$\frac{1}{|\vec{r}-\vec{r}'|} = \frac{1}{r} - \vec{r}' \cdot \nabla\frac{1}{r} + \frac{1}{2}(\vec{r}' \cdot \nabla)^2\frac{1}{r} + \cdots \tag{4.24}$$

Therefore, **Equation 3.13** can be rewritten as

$$\begin{aligned}\varphi(\vec{r}) &= \frac{1}{4\pi\varepsilon_0}\left\{\iiint_{V_1} \rho(\vec{r}')\left[\frac{1}{r} - \vec{r}' \cdot \nabla\frac{1}{r} + \frac{1}{2}(\vec{r}' \cdot \nabla)^2\frac{1}{r} + \cdots\right] dV'\right\} \\ &= \frac{1}{4\pi\varepsilon_0}\frac{1}{r}\iiint_{V_1} \rho(\vec{r}')dV' - \frac{1}{4\pi\varepsilon_0}\iiint_{V_1} \rho(\vec{r}')\vec{r}' \cdot \nabla\frac{1}{r}dV' \\ &\quad + \frac{1}{8\pi\varepsilon_0}\iiint_{V_1} \rho(\vec{r}')(\vec{r}' \cdot \nabla)^2\frac{1}{r}dV' + \cdots \end{aligned} \tag{4.25}$$

Equation 4.25 shows that the potential $\varphi(\vec{r})$ can be expressed as a series of multipole potential terms:

1) The monopole term:

$$\varphi_m(\vec{r}) = \frac{1}{4\pi\varepsilon_0}\frac{1}{r}\iiint_{V_1} \rho(\vec{r}')dV' = \frac{1}{4\pi\varepsilon_0}\frac{q}{r} \tag{4.26}$$

where $q = \iiint_{V_1} \rho(\vec{r}')dV'$ represents the total charge. This term describes the potential located at a distance r generated by a point charge, i.e., this is a monopole potential.

2) The dipole term:

$$\varphi_d(\vec{r}) = -\frac{1}{4\pi\varepsilon_0}\nabla\frac{1}{r} \cdot \iiint_{V_1} \rho(\vec{r}')\vec{r}'dV' = \frac{1}{4\pi\varepsilon_0}\frac{\vec{r}}{r^3} \cdot \iiint_{V_1} \rho(\vec{r}')\vec{r}'dV'. \tag{4.27}$$

Defined the general dipole moment $\vec{p}$ as,

$$\vec{p} = \iiint_{V_1} \rho(\vec{r}')\vec{r}'dV'. \tag{4.28}$$

The potential $\varphi_d(\vec{r})$ can be rewritten as,

$$\varphi_d(\vec{r}) = \frac{1}{4\pi\varepsilon_0}\frac{\hat{r}\cdot\vec{p}}{r^2}. \tag{4.29}$$

This term represents the potential due to an electric dipole $\vec{p}$ at distance r.

3) The quadrupole term:

$$\varphi_q(\vec{r}) = \frac{1}{4\pi\varepsilon_0}\frac{1}{2}\iiint_{V_1} \rho(\vec{r}')(\vec{r}' \cdot \nabla)^2\frac{1}{r}dV' \tag{4.30}$$

which describes the potential generated by an electric quadrupole moment $\boldsymbol{Q}$ at distance r.

Mathematical Information

Let's investigate the detailed expression for $(\vec{r}'\cdot\nabla)^2\frac{1}{r}$:

$$(\vec{r}'\cdot\nabla)^2\frac{1}{r} = \left(x'\frac{\partial}{\partial x}+y'\frac{\partial}{\partial y}+z'\frac{\partial}{\partial z}\right)^2\frac{1}{r}$$

$$= \left(x'^2\frac{\partial^2}{\partial x^2}+y'^2\frac{\partial^2}{\partial y^2}+z'^2\frac{\partial^2}{\partial z^2}+2x'y'\frac{\partial^2}{\partial x\partial y}+2y'z'\frac{\partial^2}{\partial y\partial z}+2z'x'\frac{\partial^2}{\partial z\partial x}\right)\frac{1}{r}$$

Here,

$$x'^2\frac{\partial^2}{\partial x^2}\frac{1}{r} = x'^2\frac{3x^2-r^2}{r^5}$$

$$2x'y'\frac{\partial^2}{\partial x\partial y}\frac{1}{r} = 2x'y'\frac{3xy}{r^5}$$

Without loss of generosity, we can derive other terms in above expression. Therefore,

$$(\vec{r}'\cdot\nabla)^2\frac{1}{r} = \sum_{j=1}^{3}x_j'^2\frac{3x_j^2-r^2}{r^5}+\sum_{j=1}^{3}\sum_{k\neq j}^{3}x_j'x_k'\frac{3x_jx_k}{r^5}$$

$$= \sum_{j=1}^{3}\sum_{k=1}^{3}x_j'x_k'\frac{3x_jx_k-r^2\delta_{jk}}{r^5}$$

Here x_j' and x_j represent different components of the position coordinate, i.e., $x_1'=x'$, $x_2'=y'$, $x_3'=z'$, as well as $x_1=x$, $x_2=y$, and $x_3=z$.

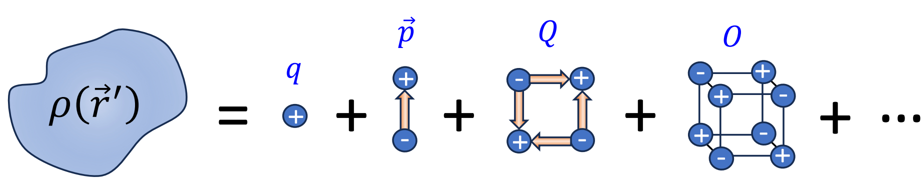


Fig. 4.6 The potential of a charged object can be treated as a superposition of potential generated by a point charge q, a dipole $\vec{p}$, a quadrupole Q, and so on.

Based on the mathematical investigation of $(\vec{r}'\cdot\nabla)^2\frac{1}{r}$, the quadrupole potential can be expressed as,

$$\varphi_q(\vec{r}) = \frac{1}{4\pi\varepsilon_0}\frac{1}{2}\iiint_{V_1}\rho(\vec{r}')\left(\sum_{j=1}^{3}\sum_{k=1}^{3}x_j'x_k'\frac{3x_jx_k-r^2\delta_{jk}}{r^5}\right)dV'$$

$$= \frac{1}{4\pi\varepsilon_0}\frac{1}{r^3}\sum_{j=1}^{3}\sum_{k=1}^{3}\frac{3x_jx_k-r^2\delta_{jk}}{r^2}\frac{1}{2}\iiint_{V_1}\rho(\vec{r}')x_j'x_k'dV'. \quad (4.31)$$

Here the quadrupole component Q_{jk} is defined as,

$$Q_{jk} = \frac{1}{2}\iiint_{V_1} \rho(\vec{r}')x_j'x_k'dV'. \tag{4.32}$$

Thus, **Equation 4.31** becomes,

$$\varphi_q(\vec{r}) = \frac{1}{4\pi\varepsilon_0}\frac{1}{r^3}\sum_{j=1}^{3}\sum_{k=1}^{3}\frac{3x_jx_k - r^2\delta_{jk}}{r^2}Q_{jk}\ . \tag{4.33}$$

Combining **Equations 4.26**, **4.29**, and **4.33**, the total potential can be expressed as,

$$\varphi(\vec{r}) = \varphi_m(\vec{r}) + \varphi_d(\vec{r}) + \varphi_q(\vec{r}) + \cdots$$

$$= \frac{1}{4\pi\varepsilon_0}\frac{q}{r} + \frac{1}{4\pi\varepsilon_0}\frac{\hat{r}\cdot\vec{p}}{r^2} + \frac{1}{4\pi\varepsilon_0}\frac{1}{r^3}\sum_{j=1}^{3}\sum_{k=1}^{3}\frac{3x_jx_k - r^2\delta_{jk}}{r^2}Q_{jk} + \cdots$$

$$= \frac{1}{4\pi\varepsilon_0}\left[\frac{q}{r} + \frac{\hat{r}\cdot\vec{p}}{r^2} + \frac{1}{r^3}\sum_{j=1}^{3}\sum_{k=1}^{3}\frac{3x_jx_k - r^2\delta_{jk}}{r^2}Q_{jk} + \cdots\right]. \tag{4.34}$$

Equation 4.34 shows that the potential generated by any arbitrary charged object can be viewed as the superposition of the potentials generated by a monopole with a charge q, a dipole with a dipole moment $\vec{p}$, a quadrupole with a quadrupole moment $\boldsymbol{Q}$, and so on, as shown in the diagram of **Figure 4.6**.

Example 4.1 *Find the electric potential of the linear and planar quadrupoles shown in* ***Figure 4.4a*** *and* ***4.4b***.

Discussion: Based on **Equation 4.33** and the corresponding calculated *Q* in **Section 4.1.2**, one shall be able to obtain the potentials generated by the linear and planar quadrupoles.

For the linear quadrupole with the quadrupole moment of **Equation 4.20**,

$$\varphi_q(\vec{r}) = \frac{1}{4\pi\varepsilon_0}\frac{1}{r^3}\sum_{j=1}^{3}\sum_{k=1}^{3}\frac{3x_jx_k - r^2\delta_{jk}}{r^2}Q_{jk} = \frac{1}{4\pi\varepsilon_0}\frac{1}{r^3}\frac{3z^2 - r^2}{r^2}Q_{zz}.$$

Since $z = r\cos\theta$, the above equation becomes,

$$\varphi_q(\vec{r}) = \frac{Q_{zz}}{4\pi\varepsilon_0 r^3}(3\cos^2\theta - 1).$$

This is the same as **Equation 4.22**.

For the planar quadrupole with the quadrupole moment of **Equation 4.23**,

$$\varphi_q(\vec{r}) = \frac{1}{4\pi\varepsilon_0}\frac{1}{r^3}\left(\frac{3zx}{r^2}Q_{zx} + \frac{3xz}{r^2}Q_{xz}\right) = \frac{Q_{xz}}{4\pi\varepsilon_0 r^3}\frac{6zx}{r^2} = \frac{3Q_{xz}}{2\pi\varepsilon_0 r^3}\sin\theta\cos\theta\sin\phi.$$

4.2.2 Multipole expansion in spherical coordinates

The core of the multipole expansion lies in how we expand $\frac{1}{|\vec{r}-\vec{r}\prime|}$ in **Equation 4.24**. In fact, one can take a different view on this expansion since

$$\frac{1}{|\vec{r}-\vec{r}\prime|}=\frac{1}{\sqrt{r^2+r\prime^2-2rr\prime\cos\theta}}=\frac{1}{r}\frac{1}{\sqrt{1-2\frac{r\prime}{r}\cos\theta+\left(\frac{r\prime}{r}\right)^2}}. \tag{4.35}$$

Here, r is the distance from the origin to the observation point, r' is the distance from the origin to the charge distribution, and θ is the angle between $\vec{r}$ and $\vec{r}'$. Recall from mathematical physics regarding the Legendre polynomial, its generating function is,

$$\frac{1}{\sqrt{1-2xt+t^2}}=\sum_{l=0}^{\infty}P_l(x)t^l. \tag{4.36}$$

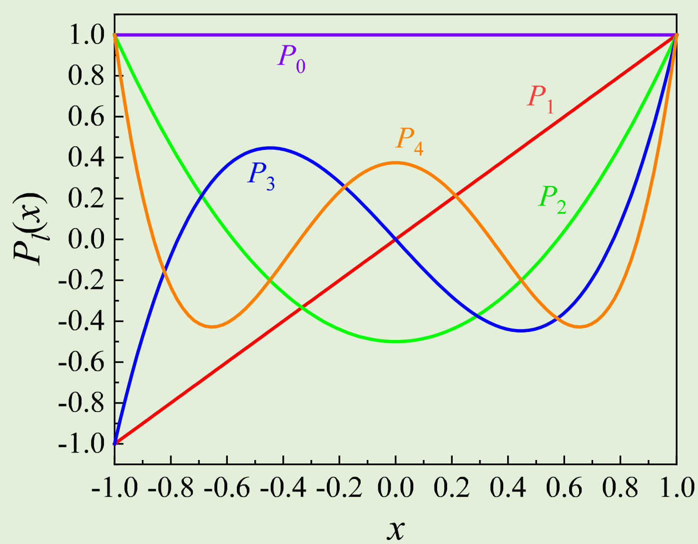
Legendre Polynomials

The first 5 Legendre polynomials ($x\in[-1,1]$) are:

$$P_0(x)=1$$
$$P_1(x)=x$$
$$P_2(x)=\frac{1}{2}(3x^2-1)$$
$$P_3(x)=\frac{1}{2}(5x^3-3x)$$
$$P_4(x)=\frac{1}{8}(35x^4-30x^2+3)$$
$$\cdots$$

Clearly,

$$P_l(-x)=(-1)^lP_l(x)$$



Comparing **Equation 4.36** to **Equation 4.35**, we can set $t = \frac{r'}{r}$ and $x = \cos\theta$. Thus, we find

$$\frac{1}{|\vec{r}-\vec{r}'|} = \frac{1}{r}\sum_{l=0}^{\infty} P_l(\cos\theta)\left(\frac{r'}{r}\right)^l. \tag{4.37}$$

Inserting **Equation 4.37** in **Equation 3.13**, we have

$$\varphi(\vec{r}) = \frac{1}{4\pi\varepsilon_0}\iiint_{V_1} \rho(\vec{r}')\frac{1}{r}\sum_{l=0}^{\infty} P_l(\cos\theta)\left(\frac{r'}{r}\right)^l dV'$$

$$= \frac{1}{4\pi\varepsilon_0 r}\sum_{l=0}^{\infty}\iiint_{V_1} \rho(\vec{r}')P_l(\cos\theta)\left(\frac{r'}{r}\right)^l dV'$$

$$= \frac{1}{4\pi\varepsilon_0 r}\left[\iiint_{V_1} \rho(\vec{r}')dV' + \iiint_{V_1} \rho(\vec{r}')P_1(\cos\theta)\frac{r'}{r}dV' + \iiint_{V_1} \rho(\vec{r}')P_2(\cos\theta)\left(\frac{r'}{r}\right)^2 dV' + \iiint_{V_1} \rho(\vec{r}')P_3(\cos\theta)\left(\frac{r'}{r}\right)^3 dV' + \cdots\right]. \tag{4.38}$$

Breaking this down, we can express the potential as a series of multipole contributions:

Monopole potential: $\varphi_m(\vec{r}) = \frac{1}{4\pi\varepsilon_0}\frac{q}{r}$. (4.26)

Dipole potential: $\varphi_d(\vec{r}) = \frac{1}{4\pi\varepsilon_0 r^2}\iiint_{V_1} \rho(\vec{r}')r'\cos\theta\, dV'$. (4.39)

Quadrupole potential: $\varphi_q(\vec{r}) = \frac{1}{4\pi\varepsilon_0 r^3}\iiint_{V_1} \rho(\vec{r}')r'^2\frac{(3\cos^2\theta-1)}{2}dV'$. (4.40)

Octupole potential: $\varphi_O(\vec{r}) = \frac{1}{4\pi\varepsilon_0 r^4}\iiint_{V_1} \rho(\vec{r}')r'^3\frac{(5\cos^3\theta-3\cos\theta)}{2}dV'$. (4.41)

…

4.2.3 The property of a general dipole

According to **Equation 4.28**, the general definition for a dipole moment is given by

$$\vec{p} = \iiint_{V_1} \rho(\vec{r}')\vec{r}'dV'. \tag{4.28}$$

The corresponding potential for a dipole in a region far from the charge distribution is

$$\varphi_d(\vec{r}) = \frac{1}{4\pi\varepsilon_0}\frac{\hat{r}\cdot\vec{p}}{r^2} \quad \text{for } r \gg R. \tag{4.29}$$

The corresponding electric field is

$$\vec{E}_d(\vec{r}) = \frac{1}{4\pi\varepsilon_0}\left[\frac{3\hat{r}(\hat{r}\cdot\vec{p})-\vec{p}}{r^3}\right] \quad \text{for } r \gg R. \tag{4.42}$$

This indicates that in the presence of an external electric field, the dipole experiences not only a direct electrostatic force but also a dipole force,

$$\vec{F}_d(\vec{r}) = \nabla\left(\vec{p} \cdot \vec{E}_{ext}\right). \tag{4.43}$$

Here $\vec{E}_{ext}$ is the external electric field applied to the dipole. The torque acting on the charged object can be written as,

$$\vec{N} = \vec{p} \times \vec{E} + \vec{r} \times \vec{F}_e. \tag{4.44}$$

Interaction energy of two dipoles

The interaction energy U_{12} between two dipoles can be calculated as

$$U_{12} = -\vec{p}_2 \cdot \vec{E}_1 = \frac{1}{4\pi\varepsilon_0}\left[\frac{\vec{p}_1\cdot\vec{p}_2 - 3(\hat{r}_{21}\cdot\vec{p}_2)(\hat{r}_{21}\cdot\vec{p}_1)}{|\vec{r}_{21}|^3}\right], \tag{4.16}$$

and the total interaction energy U_d for multiple dipoles can be expressed as,

$$U_d = \frac{1}{4\pi\varepsilon_0}\frac{1}{2}\sum_{j=1}^{N}\sum_{k\neq j}^{N}\left[\frac{\vec{p}_j\cdot\vec{p}_k - 3(\hat{r}_{kj}\cdot\vec{p}_j)(\hat{r}_{kj}\cdot\vec{p}_k)}{|\vec{r}_{kj}|^3}\right]. \tag{4.45}$$

Here $\vec{r}_{kj} = \vec{r}_k - \vec{r}_j$ and $\hat{r}_{kj} = \vec{r}_{kj}/r_{kj}$.

Dipole moment of discrete distributed charges

For a system of N point charges, with charge q_j located at $\vec{r}_j = (x_j, y_j, z_j)$, the dipole moment can be written as,

$$\vec{p} = (p_x, p_y, p_z), \tag{4.46}$$

with

$$\begin{cases} p_x = \sum_{j=1}^{N} q_j x_j \\ p_y = \sum_{j=1}^{N} q_j y_j \\ p_z = \sum_{j=1}^{N} q_j z_j \end{cases}. \tag{4.46'}$$

Electric dipole layer

An electric dipole layer can be considered as a layer of dipoles distributed on a surface. Examples include cell membranes, material interfaces, electric double layers, and colloidal particles. As shown in **Figure 4.7**, a cellular membrane often consists of lipid molecules arranged in pairs, forming a bilayer with hydrophilic ends facing outward and hydrophobic tails inward, with a thickness of approximately 5 nm. Typically, the membrane maintains an electrical potential difference across it, usually around 70 mV in animal cells. This behavior can be modeled as two parallel flat sheets with uniform charge and a constant electric field between them, where the two plates are treated as a dipole layer.

At the interface between two materials with different electrical properties, electric dipoles may be induced or aligned, commonly occurring in dielectric materials where charges within the material can separate, creating a dipole moment, details see **Chapter 6**.

In electrochemistry and colloidal science, for a charged surface immersed in an electrolyte solution, an electric dipole layer can be formed at the interface between the charged surface (solid or liquid) and an electrolyte solution. The Stern layer in the electric double layer often behaves like a layer of electric dipoles.

Considering an area S in the dipole layer, the total dipole moment can be written as $\vec{p}_S = q_S\vec{d}$. We can define a surface dipole moment density

$$\vec{\tau} = \frac{\vec{p}_S}{S} = \frac{q_S\vec{d}}{S} = \sigma\vec{d}. \tag{4.47}$$

where σ is the surface charge density. Alternatively, we can express $\vec{\tau}$ as

$$\vec{\tau} = \frac{d\vec{p}_S}{dS}. \tag{4.48}$$

Taking a small area dS as shown in **Figure 4.7b**, we can calculate the potential $d\varphi_d$ it generated at point P,

$$d\varphi_d = \frac{1}{4\pi\varepsilon_0}\frac{\vec{r}\cdot d\vec{p}}{r^3} = \frac{1}{4\pi\varepsilon_0}\frac{\vec{r}\cdot\vec{\tau}}{r^3}dS. \tag{4.49}$$

Therefore, the total potential generated by the dipole layer at location P can be written as,

$$\varphi_d = \iint_S \frac{1}{4\pi\varepsilon_0}\frac{\vec{r}\cdot\vec{\tau}}{r^3}dS. \tag{4.50}$$

The potential jump across a dipole layer is given by,

$$\Delta\varphi = E_{in}d = \frac{\tau}{\varepsilon_0}, \tag{4.51}$$

where E_{in} is the electric field between two charged layers, expressed as $E_{in} = \frac{\sigma}{\varepsilon_0}$.

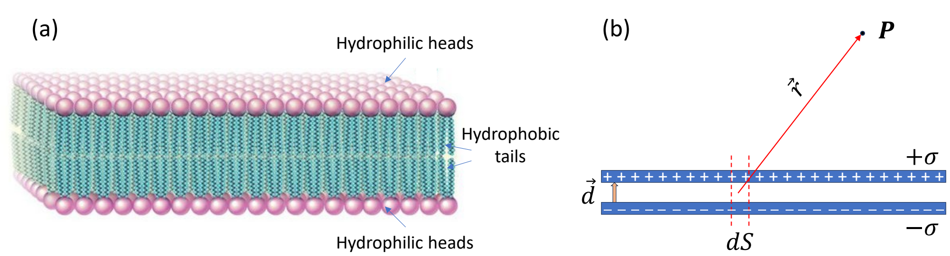


Fig. 4.7 (a) The cell membrane structure and (b) a simple bi-layer charged model.

Example 4.2 *The charge distribution of a colloidal electro-double layer: A charged colloid is immersed in a electrolyte solution, what is the charge distribution away from the surface of the colloid?*

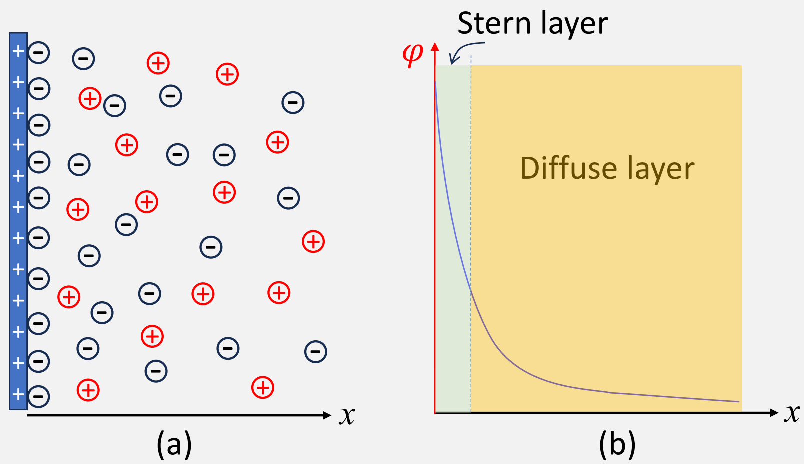


Fig. 4.8 A uniformly charged surface in an electrolyte with a charge distribution.

Discussion: Assume that the charged colloid surface is an infinitely flat surface as shown in **Figure 4.8a**, and due to electrostatic interaction, there is a charge density distribution $\rho(x)$ in the electrolyte solution. The electrostatic potential $\varphi(x)$ shall satisfy the Poisson's equation,

$$\frac{d^2\varphi(x)}{dx^2} = -\frac{\rho(x)}{\varepsilon}.$$

Let's consider how to find $\rho(x)$. If the entire system is under thermal equilibrium, the charged particle in the solution shall follow the Boltzmann distribution, i.e., the number $n(x)$ of the charged particle shall follow,

$$n(x) = n_0 e^{-U(x)/k_BT}.$$

Assume that in the electrolyte, there are two different ions, the negative ions carry a charge of $-ze$, and each positive ion has $+ze$ charge. Therefore, the electric potential energy for negative and positive ions are,

$$\begin{cases} U_+(x) = ze\varphi(x) \\ U_-(x) = -ze\varphi(x) \end{cases}.$$

Therefore, the numbers of positive and negative ions $n_\pm(x)$ can be expressed as,

$$\begin{cases} n_+(x) = n_0 e^{-ze\varphi(x)/k_BT} \\ n_-(x) = n_0 e^{ze\varphi(x)/k_BT} \end{cases}.$$

Thus, the charge density can be written as,

$$\rho(x) = zen_+(x) - zen_-(x) = en_0\left[e^{-ze\varphi(x)/k_BT} - e^{ze\varphi(x)/k_BT}\right].$$

Therefore, the Poisson's equation changes to

$$\frac{d^2\varphi(x)}{dx^2} = -\frac{zen_0}{\varepsilon}\left[e^{-\frac{ze\varphi(x)}{k_BT}} - e^{\frac{ze\varphi(x)}{k_BT}}\right] = \frac{2zen_0}{\varepsilon}\sinh\left[\frac{ze\varphi(x)}{k_BT}\right].$$

Multiply $2\frac{d\varphi}{dx}$ at both sides of above equation and integrate, we have

$$\left(\frac{d\varphi}{dx}\right)^2 = \frac{4k_BTn_0}{\varepsilon}\cosh\left[\frac{ze\varphi(x)}{k_BT}\right] + C.$$

Here C is a constant. Let's consider the boundary condition, i.e., at $x \to \infty$, $\varphi \to 0$, $\frac{d\varphi}{dx} = 0$, and consider $\cosh(0) = 1$, above equation changes to

$$\left(\frac{d\varphi}{dx}\right)^2 = \frac{4k_BTn_0}{\varepsilon}\left[\cosh\left(\frac{ze\varphi}{k_BT}\right) - 1\right].$$

Since $\cosh(2y) - 1 = 2\sinh^2 y$ and $\varphi(x)$ is a monotonical decreasing function with x, above equation can be rewritten as,

$$\frac{d\varphi}{dx} = -\left(\frac{8n_0k_BT}{\varepsilon}\right)^{1/2}\sinh\left(\frac{ze\varphi}{2k_BT}\right).$$

Integrate both sides of above equation, and we obtain the solution of above first order ordinary differentiate equation is,

$$\tanh\left(\frac{e\varphi}{4k_BT}\right) = ve^{-\kappa x}.$$

Here $\kappa = \left(\frac{n_0z^2e^2}{\varepsilon k_BT}\right)^{1/2}$ and $v = \tanh\left(\frac{e\varphi_0}{4k_BT}\right)$, where $\varphi_0 = \varphi(x = 0)$ is the potential at $x = 0$.

The above theoretical derivation and model is called Debye-Hückel theory for double layer. Based on this theory, multiple interesting properties can be obtained:

(1) *Debye Length*: The Debye length is a measure of the screening length of electrostatic interactions in the solution. It is inversely proportional to the square root of the ion concentration and is a key parameter in understanding the extent of the electrical double layer. 1 Debye length defines the thickness of the Stern layer.

(2) *Ionic Strength*: The ionic strength of a solution is a measure of the concentration of ions in the solution. The Debye-Hückel theory relates the ionic strength to the Debye length and the charge of the ions in the solution.

(3) *Potential at the Stern Layer*: The theory allows the calculation of the electric potential at the inner Helmholtz plane or Stern layer, which is the region where ions are tightly bound to the surface.

(4) *Surface Potential (ζ (zeta)-potential)*: The ζ-potential represents the electrokinetic potential at the slipping plane in the diffuse part of the electrical double layer. It is related to the surface charge and the potential drop across the diffuse layer.

(5) *Electrophoretic Mobility*: The Debye-Hückel theory provides insights into the electrophoretic mobility of charged particles in colloidal systems. It describes the motion of charged particles under the influence of an electric field.

(6) *Activity Coefficients*: The theory incorporates activity coefficients, which describe the deviation of ion behavior from ideal behavior in solutions. These coefficients are crucial for understanding the non-ideality of electrolyte solutions.

(7) *Donnan Equilibrium*: The theory can be extended to understand the Donnan equilibrium, which describes the distribution of ions between two compartments separated by a semipermeable membrane.

(8) *Dielectric Constant Effects*: The Debye-Hückel theory takes into account the dielectric constant of the medium, influencing the strength of electrostatic interactions.

Based on the potential curve $\varphi(x)$, the double layer consists of two main regions: the Stern layer (also known as the inner Helmholtz plane) and the diffuse layer. As shown in **Figure 4.8b**, the Stern layer is the region where ions are strongly adsorbed or specifically bound to the charged surface. The Stern layer is considered compact and consists of ions that are in immediate proximity to the charged surface. The adsorbed ions form a dense layer, and this region is sometimes analogously referred to as a "bound layer." Beyond the Stern layer, there is a region known as the diffuse layer, where ions are distributed more randomly and extend into the bulk solution. The diffuse layer is characterized by a decrease in ion concentration with increasing distance from the charged surface. The Stern layer, with its adsorbed ions, can be likened to a layer of dipoles formed by the aligned or oriented charges on the surface. This is analogous to a dipole layer in which charges have a specific orientation. The diffuse layer, with its distribution of ions, contributes to the overall polarization of the solution surrounding the charged surface. This polarization effect can also be represented as a layer of induced dipoles.

4.2.2 The property of a general quadrupole

Based on the electric multipole expansion, the potential generated by a quadrupole can be expressed by **Equation 4.33**,

$$\varphi_q(\vec{r}) = \frac{1}{4\pi\varepsilon_0}\frac{1}{r^3}\sum_{j=1}^{3}\sum_{k=1}^{3}\frac{3x_jx_k - r^2\delta_{jk}}{r^2}Q_{jk}\ , \tag{4.33}$$

with Q_{jk} as the component of the electric quadrupole moment,

$$Q_{jk} = \frac{1}{2}\iiint_{V_1}\rho(\vec{r}')x'_jx'_kdV'. \tag{4.32}$$

As shown in **Equation 4.32**, Q_{jk} depends solely on the charge distribution, not the coordinates chosen, which means it remains invariant under coordinate transformations. Additionally, due to the symmetrical nature of the quadrupole moment, we have the property $Q_{jk} = Q_{kj}$.

Force and Torque on the Quadrupole in an External Electric Field

When a quadrupole is placed in an external electric field $\vec{E}$, it experiences a force that can be expressed as,

$$\vec{F}_q = \sum_{j=1}^{3}\sum_{k=1}^{3} Q_{jk}\nabla_j\nabla_k\vec{E}. \tag{4.52}$$

where ∇_j and ∇_k represent the gradient operators acting on the j-th and k-th components of the electric field. This equation indicates that the force on the quadrupole is influenced by the spatial variation of the electric field, as the quadrupole moment interacts with the gradients of the electric field components.

The torque N acting on the quadrupole can be formulated as,

$$\vec{N} = 2(\boldsymbol{Q}\cdot\nabla)\times\vec{F} + \vec{r}\times\vec{F}. \tag{4.53}$$

This expression shows that the torque arises not only from the force acting on the quadrupole but also from how the quadrupole moment interacts with the electric field. The first term captures the contribution from the quadrupole moment and its interaction with the field gradients, while the second term accounts for the torque due to the force applied at a distance $\vec{r}$ from the origin.

The interaction energy U_q of the quadrupole in the external electric field can be expressed as,

$$U_q = -\sum_{j=1}^{3}\sum_{k=1}^{3} Q_{jk}\nabla_j E_k(\vec{r}). \tag{4.54}$$

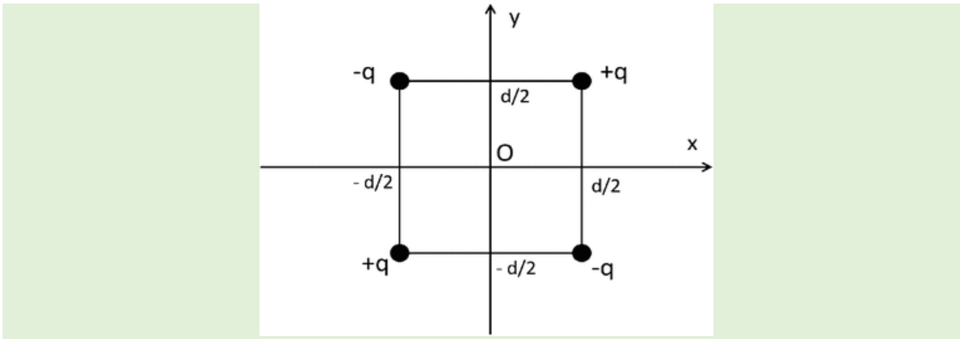
This equation illustrates that the interaction energy is a function of the quadrupole moment and the gradients of the electric field. The negative sign indicates that the system will seek a lower energy state, meaning that the quadrupole will tend to align in a way that minimizes its potential energy within the field.

In-class Activity

4-1. Derive that the energy of a point dipole in an external electric field is $U_D = -\vec{p}\cdot\vec{E}(\vec{r})$.

4-2. What is the force acting on a point dipole when it is placed in an external field $\vec{E}(\vec{r})$.

4-3. Find the electrostatic potential of the planar quadrupole.


y
-q
+q
d/2
O
x
- d/2
d/2
+q
- d/2
-q