Atomic and Molecular Polarizations
(Griffiths – Chapter 4: Section 1)

This chapter deals with electric properties of matter, loosely divided into conductors and insulators (or dielectrics). In contrast to conductors, electrons in dielectrics are attached to specific atoms or molecules. Although atoms and molecules are electrically neutral, they nonetheless exhibit intrinsic and extrinsic polarizability properties defined, respectively, in the absence or presence of an external electric field.

- **Atomic Polarizability**

  When a neutral atom is placed in an external electric field $\mathbf{E}$, the electron cloud responds by moving in the opposite direction to the electric field $\mathbf{E}$ (while the heavier positively-charged nucleus almost remains in place), thereby creating a dipole moment

  $$ p = \alpha \mathbf{E} $$

  in the same direction as the electric field $\mathbf{E}$, where the constant of proportionality is called the atomic polarizability $\alpha$. 

  ![Diagram of Atomic Polarization](image)

  Note that atomic polarizability $\alpha$ must have units $[\alpha] = [\epsilon_0] \cdot m^3$ and is a strong function of the atomic number (see Figure below).
From the Figure above, we see that alkali metals have the largest polarizabilities while the smallest values correspond to noble gases. This is simply due to their electronic configurations: alkali metals have a single electron outside of closed electronic shells while noble gases have closed electronic shells. Hence, alkali atoms are easily polarized by an external electric field while, as can be seen from the Figure above, noble-gas atoms are weakly polarizable. From the Figure above, we can check that the polarizability of noble gases scales linearly with atomic number $Z$.

The displacement shown in the first Figure above is, of course, grossly exaggerated. In fact, assuming that the electron cloud (of net charge $-q$) maintains its spherical shape (adequate for noble gases) and that the nucleus (of net charge $q$) has shifted to the right (in the direction of the electric field $E \hat{x}$) by a distance $z$, the electric field due to the electron cloud as experienced by the nucleus is

$$E_e = -\frac{qd}{4\pi\epsilon_0 a^3} \hat{x},$$

where $a$ denotes the atomic radius. Because atomic polarizability is a property of matter in equilibrium, the displacement $d$ adjusts itself so that the electron-cloud field matches the external field: $E_e = E$. Hence, the electric dipole moment $p = qd$ is now expressed as $p = 4\pi\epsilon_0 a^3 E$, which yields the following expression for the atomic polarizability

$$\frac{\alpha}{4\pi\epsilon_0} = a^3.$$

A best-fit analysis of the atomic radii of noble gases yields $a^3(Z) = (2.9 + 0.14Z) \times 10^{-30}$ m$^3$, which overestimates real atomic polarizability values for noble gases by a factor of 10 or more, although it reproduces the linear $\alpha - Z$ relationship.
In general, for a spherically-symmetric charge distribution \( \rho(r) \), the magnitude of the electric field at a distance \( z \) from the center of the distribution is

\[
E(z) = \frac{1}{\epsilon_0 z^2} \int_0^z \rho(r) r^2 dr,
\]

and the linear relation \( p = qz = \alpha E(z) \) holds for sufficiently small values of \( z \). For example, using the electronic charge distribution for a hydrogen atom \( \rho(r) = \frac{q}{\pi a_0^3} \exp\left(-\frac{2r}{a_0}\right) \),

where \( a_0 = 0.5 \times 10^{-10} \text{ m} \) denotes the Bohr radius, we find after integrating by parts

\[
E(z) = \frac{q}{4\pi \epsilon_0 z^2} \left[ 1 - e^{-2z/a_0} \left( 1 + 2 \frac{z}{a_0} + 2 \frac{z^2}{a_0^2} \right) \right],
\]

which becomes (in the limit \( z \ll a_0 \))

\[
E(z) \to \frac{4}{3} \frac{q}{4\pi \epsilon_0 \frac{z}{a_0^3}} \Rightarrow \frac{\alpha}{4\pi \epsilon_0} = \frac{3}{4} \frac{a_0^3}{a_0}.
\]

Substituting the value for the Bohr radius, we find \( \alpha/(4\pi \epsilon_0) = 0.09 \times 10^{-30} \text{ m}^3 \), compared to the experimental value \( 0.667 \times 10^{-30} \text{ m} \).

- **Molecular Polarizability**

The situation gets more complicated when one considers molecular polarizabilities. For completely asymmetrical molecules, for example, we write the dipole moment

\[
p = \alpha \cdot E\]

or

\[
\begin{pmatrix}
p_x \\
p_y \\
p_z
\end{pmatrix} = \begin{pmatrix}
\alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\
\alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\
\alpha_{zx} & \alpha_{zy} & \alpha_{zz}
\end{pmatrix} \cdot \begin{pmatrix}
E_x \\
E_y \\
E_z
\end{pmatrix},
\]

in terms of the \( 3 \times 3 \) polarizability tensor \( \alpha \), which can be diagonalized by choosing appropriate principal axes \( (\hat{1}, \hat{2}, \hat{3}) \), such that

\[
\alpha = \alpha_1 \hat{1}\hat{1} + \alpha_2 \hat{2}\hat{2} + \alpha_3 \hat{3}\hat{3},
\]

where the principal polarizabilities \( (\alpha_1, \alpha_2, \alpha_3) \) are generally different from each other. Hence, in the general asymmetric case, the dipole moment \( p \) may be written as

\[
p = \alpha_1 E_1 \hat{1} + \alpha_2 E_2 \hat{2} + \alpha_3 E_3 \hat{3},
\]

and we note that \( p \) may not be parallel to the electric field \( E \) itself since

\[
p \times E = (\alpha_2 - \alpha_3) E_2 E_3 \hat{1} + (\alpha_3 - \alpha_1) E_3 E_1 \hat{2} + (\alpha_1 - \alpha_2) E_1 E_2 \hat{3}.
\]
Many polar molecules have finite electric dipole moments $p_0$ even in the absence of an external electric field (e.g., the magnitude of the electric dipole for the water molecule is $p_0 = 6.1 \times 10^{-30}$ C\cdot m or $d_0 = p_0/e = 0.38$ Å). When a polar molecule (with electric dipole $p_0$) is placed in an external uniform electric field, the molecule experiences a torque $\mathbf{N} = p_0 \times \mathbf{E}$, which causes the dipole $p_0$ to align itself with the electric field $\mathbf{E}$ (see Figure below).

Hence, on the one hand, the net force on an electric dipole due to a uniform electric field vanishes. On the other hand, when the electric field is nonuniform, the net electric force on the dipole is

$$\mathbf{F} = \mathbf{F}_+ + \mathbf{F}_- = q \Delta \mathbf{E} = p_0 \cdot \nabla \mathbf{E} = -p_0 \cdot \nabla \nabla \Phi = \nabla \mathbf{E} \cdot p_0 = \nabla (\mathbf{E} \cdot p_0).$$

An electric dipole also acquires potential energy

$$U = -p_0 \cdot \mathbf{E}$$

when it is exposed to an external electric field. This expression is obtained by calculating the work done by the electric field $\mathbf{E} = E\hat{x}$ when the electric dipole $\mathbf{p} = p (\cos \theta \hat{x} + \sin \theta \hat{y})$ in moved from $\theta = \pi/2$ to an arbitrary angle $\theta$. Using the expression for the torque

$$\mathbf{N} = \mathbf{p} \times \mathbf{E} = -pE \sin \theta \hat{z},$$

we find

$$W = \int_{\pi/2}^{\theta} N(\theta') \, d\theta' = pE \cos \theta = U(\pi/2) - U(\theta).$$