LECTURE NOTES 9
ELECTROSTATIC FIELDS IN MATTER:
DIELECTRIC MATERIALS & THEIR PROPERTIES

Polarization

We have previously discussed the electrostatic properties of conductors of electricity. Now we wish to discuss the opposite end of the spectrum – the electrostatic properties of insulators – non-conductors (very poor conductors) of electricity.

Suppose we have a block of insulator material, or even a gas or liquid – non-conducting – consisting of atoms, or atoms bound together as molecules (e.g. H₂O, CO₂, HCOOH, etc.) Solid materials that are insulators are things like wood, plastic, glass (amorphous SiO₂), rubber, etc. All of these materials are very poor conductors of electricity – insulators. They are examples of dielectric materials, generically known as dielectrics.

An “ideal” dielectric material is one which contains no free charges. Since microscopically, the dielectric material consists of atoms, its macroscopic electrostatic dielectric properties arise from the collective (sum total) contributions of its microscopic constituents – at the atomic scale.

Each atom consists of a central, positive-charged “pointlike” nucleus (\[ R_{\text{nucleus}} \sim \text{few fermi's} \, (1 \text{fm} = 10^{-15} \text{m}) \]) surrounded by “clouds” of electrons, bound to the nucleus. The atomic electrons are not free → typical radius of orbiting electrons is \( \sim \text{few angstroms} \, (1 \text{Å} = 10^{-10} \text{m}) \) ability to move / migrate!

Polarization of an Atom in an Externally-Applied Electric Field:

First, consider an atom (electrically neutral) in its ground state (lowest quantum energy level) such as the hydrogen atom (simplest case). The single electron orbiting the nucleus (a single proton) has a spherically–symmetric charge distribution (i.e. no \( \theta \) or \( \phi \)-dependence) in the absence of any externally-applied electric field, i.e. \( E_{\text{ext}} = 0 \):

The typical electric field strength “seen” by an electron orbiting the hydrogen nucleus (a single proton) due to the nuclear electric charge is:

\[
\vec{E}_{\text{nuc}}^e(\vec{r}) = \frac{1}{4 \pi \varepsilon_o} \frac{Q_{\text{nuc.}}}{r^2} \hat{r} = \frac{1}{4 \pi \cdot 8.85 \times 10^{-12}} \frac{1.6 \times 10^{-19}}{(10^{-10})^2} \hat{r}
\]

which for \( r = 1 \text{Å} = 10^{-10} \text{m} \) gives a whopping \( |\vec{E}_{\text{nuc}}^e (r = 1 \text{Å})| = 1.44 \times 10^{11} \text{Volts} / \text{m} \) (very large!!!)

n.b. The nucleus “sees” this same electric field strength, due to the electron’s electric charge. This is a typical electric field strength internal to/in the vicinity of atoms (& molecules)!!!

Compare this internal electric field strength to the electric field strengths easily / routinely available in a laboratory setting of \( |\vec{E}_{\text{ext}}| \sim 10^3 \text{ to } 10^6 \text{ V/m} \). We realize that \( |\vec{E}_{\text{external}}| \ll |\vec{E}_{\text{internal}}| \)

i.e. \( 10^3 \text{ to } 10^6 \ll 10^{11} \text{ Volts/m} \) !!!

©Professor Steven Errede, Department of Physics, University of Illinois at Urbana-Champaign, Illinois 2005 - 2008. All rights reserved.
Because of this, when an atom (e.g. hydrogen) is placed in an external electric field, because \( E_{\text{ext}} \ll E_{\text{int}} \) the atom “sees” the externally applied field as a perturbation to its internal electric field.

Neutral atom, no externally-applied electric field:

\[
\vec{E}_{\text{ext}} = 0:
\]

![Diagram of a neutral atom with positive and negative charges and an external electric field.]  

Point-like nucleus has positive charge 
\( R_{\text{nucl}} \sim \text{few fm} \), i.e. 
\( \sim \text{few } 10^{-15} \text{ m} \)

Typical Atomic Size:

\( r_{\text{atom}} \sim \text{a few Ångstroms} \)  
\( (1 \text{ Å} = 10^{-10} \text{ m}) \)

Spherically-symmetric electron “cloud” charge distribution (negative)

**A Neutral Atom in an Externally Applied Uniform / Constant Electric Field:**

Suppose we place a neutral atom between the plates of parallel plate capacitor with e.g. \( \vec{E}_{\text{ext}} = E_o \hat{x} = 1000 \text{ Volts/meter} \) in gap-region of capacitor plates:

Atomic nucleus feels a net force of: 
\[
\vec{F}_{\text{nucl}} = Q_{\text{nucl}} \vec{E}_{\text{ext}} = +e E_o \hat{x}
\]

Electron “cloud” feels a net force of: 
\[
\vec{F}_{e} = Q_e \vec{E}_e = -e E_o \hat{x}
\]

Thus we see that: 
\[
\vec{F}_e = -\vec{F}_{\text{nucl}} = -e E_o \hat{x} \text{ (forces are equal & opposite – i.e. Newton’s 1\textsuperscript{st} Law!)}
\]

![Diagram of a neutral atom with positive and negative charges and an external electric field.]  

Electron “Cloud”, w/ Electric Charge \(-e\)
The net effect of the externally-applied electric field \( \vec{E}_{ext} = E_o \hat{x} \) is that the nucleus is displaced a tiny amount (a small fraction of size of atom) from its \( \vec{E}_{ext} = 0 \) position in the \( +\hat{x} \) direction, and the centroid (i.e. center) of the electron “cloud” is displaced a tiny amount (n.b. the size / magnitude of the displacement of centroid of electron cloud is the same as that for nucleus) from its \( \vec{E}_{ext} = 0 \) position in the \( -\hat{x} \) direction:

- Obviously, because the electrons of the atom are bound to the nucleus, the mutual attraction of the atomic Coulomb force keeps the atom together – electron cloud is bound to nucleus.
- Thus, because of the displacement of \( +Q_{nuc} \) (\( = +e \) for hydrogen) in the \( +\hat{x} \)-direction by an amount \( d/2 \) and the displacement of the centroid of the electron “cloud” charge distribution (\( Q_e = -e \) for hydrogen) to the \( -\hat{x} \) direction also by an amount \( d/2 \), caused by the application of the externally-applied uniform / constant electric field \( \vec{E}_{ext} = E_o \hat{x} \) we see that an electric dipole moment \( \vec{p} = Qd \hat{d} = Qd\hat{x} \) is induced (i.e. created) in the atom by the application of the external electric field \( \vec{E}_{ext} = E_o \hat{x} \).

Because \( |\vec{E}_{ext}| \approx 10^{-6} \ll |\vec{E}_{int}| \approx 10^{11} \) Volts/meter, the externally-applied field \( \vec{E}_{ext} \) is seen as a (very) small perturbation on the internal electric field \( \vec{E}_{int} \); hence a linear relationship exists between the induced electric dipole moment \( \vec{p} \) and the externally-applied electric field \( \vec{E}_{ext} \):

\[
\vec{p} = \alpha \vec{E}_{ext}
\]

\( \alpha \) is known as the atomic electric polarizability.
SI units of atomic polarizability: 

\[
\alpha = \frac{\bar{p}}{E_{\text{ext}}} \Rightarrow \frac{\text{Coulomb} - \text{meters}}{\text{Newtons} / \text{Coulomb}} = \frac{\text{Coulombs}^2}{\text{Newtons} / \text{m}}
\]

The atomic polarizabilities \( \alpha \) of atoms are often expressed in terms of \( \alpha/4\pi\varepsilon_o \), which has SI units of \( \alpha/4\pi\varepsilon_o \sim \ell^3 = \text{meters}^3 \), since \( \varepsilon_o = 8.85 \times 10^{-12} \text{ Farads} / \text{m} \) (= Coulombs / Newton – m²)

The table below summarizes the (normalized) atomic polarizabilities \( \alpha/4\pi\varepsilon_o \) of some of the lighter atoms, in units of \( 10^{-30} \text{ m}^3 \).

<table>
<thead>
<tr>
<th>Atomic Element</th>
<th>Nuclear Charge</th>
<th>( \alpha/4\pi\varepsilon_o )</th>
<th># e− in outer shell</th>
<th>electron configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Alkali” (single e− in outer shell)</td>
<td>H 1</td>
<td>0.667</td>
<td>“1”</td>
<td>1s ( ) denotes closed shell</td>
</tr>
<tr>
<td>Noble Gas (closed shells)</td>
<td>He 2</td>
<td>0.205</td>
<td>(closed shells)</td>
<td>(1s²)</td>
</tr>
<tr>
<td>Alkali (single e− in outer shell)</td>
<td>Li 3</td>
<td>24.3</td>
<td>1</td>
<td>(1s²) 2s</td>
</tr>
<tr>
<td></td>
<td>Be 4</td>
<td>5.60</td>
<td>( )</td>
<td>(1s²) (2s²)</td>
</tr>
<tr>
<td></td>
<td>C 6</td>
<td>1.76</td>
<td>( )</td>
<td>(1s²) (2s²) 2p</td>
</tr>
<tr>
<td>Noble Gas (closed shells)</td>
<td>Ne 10</td>
<td>0.396</td>
<td>(closed shells)</td>
<td>(1s²) (2s²) (2p⁶)</td>
</tr>
<tr>
<td>Alkali (single e− in outer shell)</td>
<td>Na 11</td>
<td>24.1</td>
<td>1</td>
<td>(1s²) (2s²) (2p⁶) 3s</td>
</tr>
<tr>
<td>Noble Gas (closed shells)</td>
<td>Ar 18</td>
<td>1.64</td>
<td>(closed shells)</td>
<td>(1s²)(2s²)(2p⁶)(3s²)(3p⁶)</td>
</tr>
<tr>
<td>Alkali (single e− in outer shell)</td>
<td>K 19</td>
<td>43.4</td>
<td>1</td>
<td>(1s²)(2s²)(2p⁶)(3s²)(3p⁶)4s</td>
</tr>
<tr>
<td>Alkali (single e− in outer shell)</td>
<td>Cs 55</td>
<td>59.6</td>
<td>1</td>
<td>(1s²)(2s²)(2p⁶)(3s²)(3p⁶)(4s²)</td>
</tr>
<tr>
<td></td>
<td><em>4p⁶</em>(5s²)(5p⁶)6s</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
It can be seen that atomic polarizability $\alpha$ has dependence on outer-most shell/valence electron! (i.e. the least tightly bound electron to nucleus - due to screening effects of inner shell electrons).

It is (certainly) possible to obtain a theoretical relation - i.e. a theoretical “pre-diction” (technically, a post-diction) of the atomic polarizability, $\alpha$ for a given atom (or molecule) relating how $\vec{p}$ (the induced electric dipole moment) depends on $E_{\text{ext}}$ (the applied external electric field). In order to do this, must “know” the atomic electron volume charge distribution / electric charge density $\rho(\vec{r})$.

Griffiths Example 4.1, pages 161-62:

A crude model for atom, due to J.J. Thompson (c.a. ~ 1910) is his “plum pudding” model of the atom – i.e. a point nucleus of positive charge $+Q$ surrounded by a uniformly charged spherical electron cloud of total charge $-Q$ of radius $a$. This means assuming a constant volume charge density $\rho_{\text{atomic}}$ for the atomic electrons orbiting the nucleus – i.e. one which is flat, out to a radius $r = a$ (and zero after that) as shown in the figure below:

\[
\rho_{\text{atomic}} = \frac{-3Q}{4\pi a^3} \text{ (Coulombs/m}^3)\]

\[
\rho_{\text{atomic}} = \frac{-Q}{V_{\text{atom}}} = \frac{-Q}{\left(\frac{4}{3}\pi a^3\right)}
\]

\[
\rho_{\text{atomic}} = \frac{-3Q}{4\pi a^3} \text{ (Coulombs/m}^3)\]
This is a (crude, but simple) theoretical model of an actual atom (i.e. far from reality), but it works somewhat well - i.e. it is accurate to a factor of \( \approx 4.5 - c.f. \) with actual data – see below!

If the nucleus is displaced a relative distance \( d \) from the centroid of the atomic electron charge density distribution, then the electric field intensity that the nucleus “sees” at that point is:

\[
\mathbf{E}_{\text{nucl}}(\mathbf{r}) = \frac{1}{4\pi\varepsilon_0} \int \rho(\mathbf{r}') \left( \frac{\mathbf{r}}{r^2} \right) d\mathbf{r}'
\]

where \( \rho(\mathbf{r}') = \rho_{\text{atomic}}(\mathbf{r}') = -\frac{3Q}{4\pi a^3} \) is constant, for \( r \leq a \).

\( 
\mathbf{r} = \mathbf{r} - \mathbf{r}' = \mathbf{d} - \mathbf{r}' = d\hat{x} - \mathbf{r}' \\
(\text{since here: } \mathbf{d} = d\hat{x})
\)

Then: 
\( r^2 = (d-x')^2 + y'^2 + z'^2 \)

The source point \( \mathbf{r}' \) moves around the interior of the spherically-symmetric atomic electron charge density “cloud” in carrying out the above volume integral.

One can see that explicitly doing this volume integral is a pain – it certainly can be done though! However, by use of the divergence theorem, we find there is an easier way to obtain what we want \( \mathbf{E}_{\text{nucl}}(\mathbf{r}) \) from Gauss’ Law:

\[
\int_V \nabla \cdot \mathbf{E}(\mathbf{r}) \, d\mathbf{r}' = \oint_S \mathbf{E}(\mathbf{r}) \cdot d\mathbf{A} = \frac{Q_{\text{encl}}}{\varepsilon_0}
\]

So we take a fictitious, spherical Gaussian surface \( S \) of radius \( d < a \) centered on the centroid of the spherically-symmetric atomic electron charge density distribution as shown below:

Then: 
\( Q_{\text{encl}} = \text{charge enclosed by } S, \text{ radius } d \)

\[
Q_{\text{encl}} = \rho V = \left( -\frac{3Q}{4\pi a^3} \right) \left( \frac{4\pi d^3}{3} \right)
\]

\[
Q_{\text{encl}} = -\frac{Q}{a^3} d^3
\]

\[
\oint_S \mathbf{E}_{\text{nucl}}(\mathbf{r}) \cdot d\mathbf{A} = \left[ \mathbf{E}_{\text{nucl}}(\mathbf{r}) \right] \frac{4\pi d^2}{\varepsilon_0}
\]

Then: 
\( \mathbf{E}_{\text{nucl}}(r = d) = \frac{-Q}{4\pi d^2} \frac{1}{\varepsilon_0} \hat{r} \) (\( \hat{r} \) direction is due to intrinsic symmetry of problem)
@ Nucleus, i.e. \( \vec{r} = \vec{d} = d\hat{x} \):
\[
\vec{E}_{\text{internal}}^{\text{nucl}} (\vec{r} = \vec{d}) = -\frac{Qd}{4\pi \varepsilon_0 a^3} \hat{x}
\]

Now the force on the nucleus due to the centroid-displaced spherically-symmetric atomic electron charge distribution is:
\[
Q_{\text{nucl}} = +Q: \quad \vec{F}_{\text{internal}}^{\text{nucl}} (\vec{r} = \vec{d}) = Q_{\text{nucl}} \vec{E}_{\text{internal}}^{\text{nucl}} (\vec{r} = \vec{d}) = -\frac{Q^2 d}{4\pi \varepsilon_0 a^3} \hat{x}
\]

Since this is an electrostatics problem, this force on the nucleus must be precisely balanced by the force on it due to the externally applied field, i.e.

\[
\vec{F}_{\text{internal}}^{\text{nucl}} (\vec{r} = \vec{d}) = Q_{\text{nucl}} \vec{E}_{\text{external}}^{\text{nucl}} (\vec{r} = \vec{d}) = Q_{\text{nucl}} E_o \hat{x} \quad \vec{E}_{\text{external}} = E_o \hat{x}
\]

\[
\vec{F}_{\text{internal}}^{\text{nucl}} (\vec{r} = \vec{d}) \quad Q_{\text{nucl}} \quad \vec{F}_{\text{external}}^{\text{nucl}} (\vec{r} = \vec{d}) \hat{x}
\]

i.e. \( \vec{F}_{\text{internal}}^{\text{nucl}} (\vec{r} = \vec{d}) + \vec{F}_{\text{external}}^{\text{nucl}} (\vec{r} = \vec{d}) = 0 \) \( \Rightarrow m_{\text{nucl}} \ddot{a}_{\text{nucl}} = 0 \) \( \Rightarrow \ddot{a}_{\text{nucl}} = 0 \)

\[
\therefore \vec{F}_{\text{external}}^{\text{nucl}} (\vec{r} = \vec{d}) = -\vec{F}_{\text{internal}}^{\text{nucl}} (\vec{r} = \vec{d})
\]

\[
\varrho_{\text{nucl}} \vec{E}_{\text{external}}^{\text{nucl}} (\vec{r} = \vec{d}) = -\varrho_{\text{nucl}} \vec{E}_{\text{internal}}^{\text{nucl}} (\vec{r} = \vec{d}) \quad \text{or:} \quad \vec{E}_{\text{external}}^{\text{nucl}} (\vec{r} = \vec{d}) = -\vec{E}_{\text{internal}}^{\text{nucl}} (\vec{r} = \vec{d}) + \frac{Qd}{4\pi \varepsilon_0 a^3} \hat{x}
\]

But: \( p = |\vec{p}| = Qd \)

\[
\therefore \quad \left| \vec{E}_{\text{external}}^{\text{nucl}} (\vec{r} = \vec{d}) \right| = \frac{p}{4\pi \varepsilon_0 a^3}
\]

Turning this around: \( p = (4\pi \varepsilon_0 a^3) E_{\text{external}} \)

\[
\therefore \quad \alpha_{\text{pp}} = \frac{p}{E_{\text{external}}} = 4\pi \varepsilon_0 a^3 \quad \Rightarrow \text{Theoretical “post-diction” for } \alpha \text{ using J.J. Thompson’s “plum-pudding” model of an atom (ca ~ 1910)}
\]

A better theoretical model of the atom: use the Schroedinger Wave Equation (i.e. use quantum mechanics) which describes the wave-nature of electrons bound to the heavy / massive “point-like” nucleus.

Electron wave function (“probability amplitude”)

Appropriate Hamiltonian Operator

Energy Eigenvalue(s) Energy spectrum of electrons bound to nucleus

\[ \psi (r, \theta, \varphi) = R(r) Y(\theta, \varphi) \]

Spherical harmonic
Electron Probability Density:
\[
P(r, \theta, \varphi) = \psi^* (r, \theta, \varphi) \psi (r, \theta, \varphi) = |\psi (r, \theta, \varphi)|^2
\]

Electron Volume Charge Density:
\[
\rho_{\text{atomic}}^1 (r, \theta, \varphi) = -e |\psi_{1,0,0} (r, \theta, \varphi)|^2
\]

For an atomic electron in the lowest energy / ground state of e.g. the hydrogen atom:

\[
\rho_{\text{atomic}}^{1,0,0} (r, \theta, \varphi) = -e |\psi_{1,0,0} (r, \theta, \varphi)|^2
\]

Ground state: \( n, l, m = 1, 0, 0 \)

Principal quantum #
Total orbital angular
(=Radial quantum #) momentum \( L \) quantum #

For hydrogen atom in its ground state:
\[
\psi_{1,0,0} (r, \theta, \varphi) = \frac{1}{\sqrt{\pi a_o^3}} e^{-r/a_o}
\]

(n.b. spherically symmetric!)

Where:
\[
a_o = \text{Bohr radius} = \left( \frac{4\pi \varepsilon_o}{e^2} \right) \left( \frac{hc}{m_e c^2} \right) = \frac{hc}{\alpha_{em} m_e c^2} = 0.53 \, \text{Å} = 0.53 \times 10^{-10} \, \text{m}
\]

And where:
\[
h = \text{Planck’s constant} = 6.626 \times 10^{-34} \, \text{Joule-sec}
\]
\[
h \equiv \frac{h}{2\pi} = 1.054 \times 10^{-34} \, \text{Joule-sec}
\]
\[
\alpha_{em} = \text{fine structure "constant"} = \frac{e^2}{4\pi \varepsilon_o} \left( \frac{1}{hc} \right) = \frac{1}{137.036}
\]
\[
(\alpha_{em} = \text{EM interactions’ dimensionless coupling strength})
\]

And:
\[
hc = 197.327 \, \text{MeV - fm} \quad (1 \, \text{MeV} = 10^6 \, \text{electron volts}, 1 \, \text{fm} = 10^{-15} \, \text{m})
\]

Rest mass energy of electron:
\[
m_e c^2 = 0.511 \, \text{MeV}
\]

And:
\[
c = \text{speed of light} = 3 \times 10^8 \, \text{meters / sec}
\]

.: For an atomic electron in the lowest energy / ground state of e.g. the hydrogen atom, the electron volume charge density is:

\[
\rho_{\text{atomic}}^{1,0,0} (r, \theta, \varphi) = -e |\psi_{1,0,0} (r, \theta, \varphi)|^2 = \frac{-e}{\pi a_o^3} e^{-r/a_o}
\]

If we use \( \rho_{\text{atomic}}^{1,0,0} (r, \theta, \varphi) = \frac{-e}{\pi a_o^3} e^{-r/a_o} \) and Gauss’ Law \( \int_{S'} \vec{E} \cdot d\vec{A} = \frac{Q_{\text{enc}}}{\varepsilon_o} \) for a Gaussian sphere of radius \( r = d \) centered on the centroid of the atomic electron charge density distribution, the result from this more sophisticated / quantum-mechanically motivated model, for the atomic polarizability \( \alpha_{\text{QM}} \) is:

\[
\alpha_{\text{QM}} = \frac{p}{E_{\text{ext}}} = 3\pi \varepsilon_o a_o^3 \quad \Rightarrow \quad \alpha_{\text{QM}} = \frac{3}{4} a_o^3 = 0.112 \times 10^{-30} \, \text{m}^3
\]

See also Griffiths problem 4.2

Compare this to J.J. Thompson’s (relatively crude/simple) “plum-pudding” model of the atom, with electron volume charge density \( \rho_{\text{atomic}} = -\frac{3e}{4\pi a_o^3} \) = constant, and with \( a = a_o \), which gave:
\[
\alpha_{pp} = \frac{p}{E_{\text{ext}}} = 4\pi\varepsilon_o a_o^3 \quad \Rightarrow \quad \frac{\alpha_{pp}}{4\pi\varepsilon_0} = a_o^3 = 0.149 \times 10^{-30} \text{ m}^3
\]

They differ by \(\sim 30\%\) from each other (for the hydrogen atom / simplest atom) - not bad for J.J.!! However, compare these two “postdictions” e.g. to the actual experimental measurement for (supposedly \textit{atomic}, i.e. not \textit{molecular}) Hydrogen (from the above table):

\[
\frac{\alpha_{\text{H}_2}^{\text{exp}}}{4\pi\varepsilon_0} = 0.667 \times 10^{-30} \text{ m}^3
\]

which is \(4.5 \times \rightarrow 6 \times\) larger than that predicted by either theory!!!

\[\Rightarrow \text{Eeek}!!! \leftrightarrow\]

Note that when \(|\vec{E}_{\text{ext}}|\) becomes comparable to, or larger than, \(|\vec{E}_{\text{internal}}|\) then there no longer exists a linear relationship between \(\vec{p}\) and \(\vec{E}_{\text{ext}}\). It becomes increasingly \textit{non}-linear:

i.e. \(\vec{p} = \alpha_0 \vec{E}_{\text{ext}} \) linear \(+ \beta \vec{E}_{\text{ext}}^2 \) quadratic \(+ \gamma \vec{E}_{\text{ext}}^3 \) cubic \(\ldots \) \textit{H.O.T.'s}

(See S.Errede’s UIUC Physics 406POM lecture notes on distortion for more details if interested.)

\textbf{Electrostatic Molecular Polarizability}

Molecules, consisting of groups of (two or more) atoms bound together (by the electromagnetic force / interaction), because of their intrinsic individual atomic structure, are often highly \textit{non}-spherical in their geometrical shapes / configurations.

- An example of one such highly non-spherical molecule is the (linear) carbon dioxide (CO\textsubscript{2}) molecule:

Because of its shape (linear, and axially-symmetric) it should come as no surprise that:

\[
\begin{pmatrix}
\text{(Molecular polarizability)} \\
\text{|| to CO}_2 \text{ molecule axis}
\end{pmatrix}
> \begin{pmatrix}
\text{(Molecular polarizability)} \\
\text{\perp to CO}_2 \text{ molecule axis}
\end{pmatrix}
\]

i.e.

\[
\alpha_{\parallel}^{\text{CO}_2} = 4.5 \times 10^{-40} \text{ cm}^3/\text{N/m} > \alpha_{\perp}^{\text{CO}_2} = 2.0 \times 10^{-40} \text{ cm}^3/\text{N/m}
\]

or:

\[
\frac{\alpha_{\parallel}^{\text{CO}_2}}{\alpha_{\perp}^{\text{CO}_2}} = \frac{4.5}{2.0} = 2.25
\]
Thus for non-spherical molecules, the net induced electric dipole moment \( \vec{p}_{\text{mol}} \) may not be parallel to \( \vec{E}_{\text{ext}} \), i.e. \( \vec{p}_{\text{mol}} \neq \alpha_{\text{mol}} \vec{E}_{\text{ext}} \).

Rather, a more correct mathematical description (i.e. for the more general case), one that does properly relate \( \vec{p}_{\text{mol}} \) to \( \vec{E}_{\text{ext}} \) is given by:

\[
\vec{p}_{\text{mol}} = \vec{\alpha}_{\text{mol}} \vec{E}_{\text{ext}}
\]

\[
\vec{\alpha}_{\text{mol}} = \begin{pmatrix}
\alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\
\alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\
\alpha_{zx} & \alpha_{zy} & \alpha_{zz}
\end{pmatrix}
\]

Now \( \hat{z} \) is the symmetry axis of molecule. It is always possible to choose the principal axes \( \hat{x}, \hat{y}, \hat{z} \) of the molecule such that off-diagonal elements of \( \vec{\alpha}_{\text{mol}} \) vanish (i.e. \( \alpha_{xy}, \alpha_{yz}, \alpha_{zx} \), etc.)

For the linear, axially-symmetric CO\(_2\) molecule, \( \alpha_{zz} = \alpha_{\parallel} \) and \( \alpha_{xx} = \alpha_{yy} = \alpha_{\perp} \).

Writing things out completely:

\[
\begin{align*}
p_x &= \alpha_{xx} E_{xx} + \alpha_{yx} E_{yx} + \alpha_{xz} E_{xz} = \alpha_{xx} E_{x} = \alpha_{\parallel} E_{x} \\
p_y &= \alpha_{yx} E_{xx} + \alpha_{yy} E_{yy} + \alpha_{yz} E_{yz} = \alpha_{yy} E_{y} = \alpha_{\parallel} E_{y} \\
p_z &= \alpha_{xz} E_{xx} + \alpha_{yz} E_{yy} + \alpha_{zz} E_{xz} = \alpha_{zz} E_{z} = \alpha_{\parallel} E_{z}
\end{align*}
\]

\[
\vec{p}_{\text{mol}} = \vec{\alpha}_{\text{mol}} \vec{E}_{\text{ext}}
\]

### Alignment (Polarization) of Polar Molecules in an Externally-Applied Electrostatic Field

A neutral atom has (and many types of neutral molecules have) no intrinsic, permanent electric dipole moment – i.e. if \( \vec{E}_{\text{ext}} = 0 \) then \( \vec{p}_{\text{atom}} \) (or \( \vec{p}_{\text{mol}} \)) = 0. Such molecules are known as non-polar molecules. However, when an external electric field is applied \( \vec{E}_{\text{ext}} \neq 0 \), then \( \vec{p}_{\text{atom}} \) (or \( \vec{p}_{\text{mol}} \)) \( \neq 0 \). Such electric dipole moments are known as induced electric dipole moments.

Some molecules, such as the all-important water molecule (H\(_2\)O) actually do have permanent electric dipole moments (i.e. even when \( \vec{E}_{\text{ext}} = 0 \), \( \vec{p}_{\text{mol}} \neq 0 \)!) The non-vanishing permanent electric dipole moment for some molecules arises because of how outer-shell atomic electrons are (non-democratically) shared amongst the individual atoms making up the molecule.

For example, in the water molecule (H\(_2\)O) the outer-shell (most loosely-bound) atomic electrons tend to cluster preferentially around the oxygen atom, and since the H\(_2\)O molecule is not axially symmetric (the two hydrogen atoms form an opening angle between them of 105° with oxygen atom at the vertex) leaving net negative charge at oxygen vertex and net positive charge at hydrogen atom end.
Molecules with permanent electric dipole moments are known as **polar molecules**. (e.g. water, benzene, toluene, . . . )

If polar molecules, with permanent electric dipole moments are placed in a uniform applied external field $\vec{E}_{ext}$, two things can/will happen:

1.) Permanent electric dipole moments tend to align / line-up with the external field:

\[
\vec{p}_{mol}^{\text{permanent}} \parallel \vec{E}_{ext}
\]

2.) The external applied electric field $\vec{E}_{ext}$ can / does induce a (non-permanent) electric dipole moment:

\[
\vec{p}_{mol}^{\text{induced}} = \alpha_{mol} \vec{E}_{ext}
\]

Thus:

\[
\vec{p}_{mol}^{\text{total}} = \vec{p}_{mol}^{\text{permanent}} + \vec{p}_{mol}^{\text{induced}} = \vec{p}_{mol}^{\text{permanent}} + \alpha_{mol} \vec{E}_{ext}
\]

Usually, for typical values of $|\vec{E}_{ext}| \sim 1000$ Volts/meter, thus $|\vec{p}_{mol}^{\text{induced}}| \ll |\vec{p}_{mol}^{\text{permanent}}|$ for polar molecules with permanent electric dipole moments. Why?? Because $|\vec{E}_{\text{internal}}^{\text{atomic}}| \gg |\vec{E}_{ext}|$.

So to “zeroth order” when a molecule with a permanent electric dipole moment is placed in an external electric field $\vec{E}_{ext}$:

\[
\vec{p}_{mol}^{\text{total}} \approx \vec{p}_{mol}^{\text{permanent}} \quad \text{because} \quad |\vec{p}_{mol}^{\text{induced}}| \ll |\vec{p}_{mol}^{\text{permanent}}| \quad \text{if} \quad |\vec{E}_{\text{internal}}^{\text{atomic}}| \gg |\vec{E}_{ext}|.
\]
What happens when polar molecules (and/or pure physical electric dipoles) are placed in a uniform external electric field $\vec{E}_{ext}$?

$\vec{F}_+ = +Q\vec{E}_{ext} = +QE_o\hat{x}$

$\vec{F}_- = -Q\vec{E}_{ext} = -QE_o\hat{x}$

$\vec{F}_{net} = \vec{F}_+ + \vec{F}_- = +Q\vec{E}_{ext} - Q\vec{E}_{ext} = 0$

→ $\exists$ No net force on polar molecular dipole!!! (for uniform / constant $\vec{E}_{ext} = E_o\hat{x}$)

However, $\exists$ a net torque on the polar molecular dipole: $\vec{N} = \vec{r} \times \vec{F}$

The net torque acting on the polar molecular dipole is:

$\vec{N}_{net} = \vec{N}_+ + \vec{N}_- = (\vec{r} \times \vec{F}_+) + (\vec{r} \times \vec{F}_-)$

Take torques about the midpoint $O$ of dipole

$\vec{N}_{net} = \frac{\vec{d} \times \vec{F}_+}{2} + \frac{-\vec{d} \times \vec{F}_-}{2}$

$= \frac{\vec{d} \times Q\vec{E}_{ext}}{2} + \frac{-\vec{d} \times -Q\vec{E}_{ext}}{2}$

$= Q\left(\frac{\vec{d} \times \vec{E}_{ext}}{2}\right)$ but $\vec{p} = Q\vec{d}$

Thus: $\vec{N}_{net} = \vec{p} \times \vec{E}_{ext}$

And: $|\vec{N}_{net}| = pE_{ext} \sin \Theta = pE_o \sin \Theta$

n.b.: $\vec{N}_{net}$ points in direction $(\hat{d} \times \hat{x})$

(Use right-hand rule for $\times$-product!!!)
The torque $\vec{N}_{net}$ acting on the electric dipole (with pure electric dipole moment $\vec{p} = Q\vec{d}$) due to uniform / constant electric field $\vec{E}_{ext} = E_o \hat{x}$ acts such that $\vec{p}$ lines up parallel to $\vec{E}_{ext}$. The polar molecule is free to rotate, and will do so until $\vec{p} \parallel \vec{E}_{ext} = E_o \hat{x}$, as shown below:

**$E$-field-aligned polar molecule / electric dipole moment $\vec{p}$**:

- n.b. when polar molecule / electric dipole moment $\vec{p}$ is aligned with $\vec{E}_{ext}$, note that the net torque on the dipole, $\vec{N}_{net}$ vanishes: $\vec{N}_{net} = Q\vec{d} \times \vec{E}_{ext}$ but when $\vec{d} \parallel \vec{E}_{ext}$ the cross product vanishes! $|\vec{N}_{net}| = 0 = pE_o \sin \Theta$ because $\Theta = 0$ when $\vec{p} \parallel \vec{E}_{ext} = E_o \hat{x}$.

- We have shown (P435 Lect. Notes 8) that the potential energy $U_p$ of a pure electric dipole $\vec{p}$ in an external electric field $\vec{E}_{ext}$ is:

$$W = P.E. = -\vec{p} \cdot \vec{E}_{ext} = -pE_{ext} \cos \Theta$$

Work/Potential Energy vs. Angle $\Theta$ of Electric Dipole In External Electric Field:
What happens to polar molecules (and/or pure physical electric dipoles) when they are placed in a non-uniform externally-applied electric field $\vec{E}_{ext}$?

\[ \vec{E}_{ext} = -\frac{1}{4\pi\varepsilon_0} \frac{Q}{r} \hat{r} \Rightarrow \text{polar molecule in } E\text{-field associated with a point charge, } -Qs: \]

![Diagram of electric field and dipole](image)

Force on $+Q$: $\vec{F}_+ (\vec{r}_+) = +Q\vec{E}_{ext} (\vec{r}_+)$

Force on $-Q$: $\vec{F}_- (\vec{r}_-) = -Q\vec{E}_{ext} (\vec{r}_-)$

But here: $\vec{E}_{ext} (\vec{r}_+) \neq \vec{E}_{ext} (\vec{r}_-)$!!!

Net Force on dipole: $\vec{F}_{net} = \vec{F}_+ (\vec{r}_+) + \vec{F}_- (\vec{r}_-) = +Q\vec{E}_{ext} (\vec{r}_+) - Q\vec{E}_{ext} (\vec{r}_-)$

$\vec{F}_{net} = Q(\vec{E}_{ext} (\vec{r}_+) - \vec{E}_{ext} (\vec{r}_-))$

$\vec{F}_{net} = Q\Delta\vec{E}_{ext}$ where $\Delta\vec{E}_{ext} \equiv (\vec{E}_{ext} (\vec{r}_+) - \vec{E}_{ext} (\vec{r}_-))$

For polar molecules $|\vec{d}| = |\vec{r}_+ - \vec{r}_-| \sim \text{few } \text{Ångstroms} - \text{typical atomic distance scale}!!!$

Thus, since $|\vec{d}|$ is so small, here we may use: $\Delta\vec{E}_{ext} = (\vec{d} \cdot \vec{\nabla})\vec{E}_{ext}$

\[
\begin{align*}
\Delta E_x & = \vec{\nabla} E_{ext} \cdot \vec{d} \\
\Delta E_y & = \vec{\nabla} E_{ext} \cdot \vec{d} \\
\Delta E_z & = \vec{\nabla} E_{ext} \cdot \vec{d}
\end{align*}
\]

See Griffiths equation 1.35

\[ \vec{F}_{net} = (\vec{p} \cdot \vec{\nabla})\vec{E}_{ext} \]

n.b. $\vec{F}_{net} = m_{dipole} \vec{a}_{dipole}$ (Newton’s 2nd Law of Motion)

⇒ If external field $\vec{E}_{ext}$ is non-uniform, a net force exists on an electric dipole/polar molecule which is proportional to the spatial gradient of the externally applied electric field $\vec{\nabla}\vec{E}_{ext}$ which causes the dipole/polar molecule to accelerate!
Suppose we have a polar liquid – e.g. water (H2O) with $p_{mol} = p_{H2O} = 6.1 \times 10^{-30}$ coulomb-meters permanent electric dipole moment for each / associated with each water molecule.

Why don’t polar water molecules spontaneously align with each other, thereby minimizing their overall energy?? (e.g. like magnetic dipoles (atomic) inside a permanent magnet)

Consider a universe in which there are only two such polar molecules (and nothing else). Then the overall/total potential energy (by the Principle of Linear Superposition) is:

$$W_{p_1,p_2} = P.E. = U_{p_1} + U_{p_2} = -\vec{p}_1 \cdot \vec{E}_2(\vec{r}_1) - \vec{p}_2 \cdot \vec{E}_1(\vec{r}_2)$$

$\vec{E}_1$-field of dipole1 (@ dipole2 $(\vec{r}_2)$)

$\vec{E}_2$-field of dipole2 (@ dipole1 $(\vec{r}_1)$)

Define: $\vec{r}_2 = -\vec{r}_1$

$\vec{E}_2$-field of dipole2 (@ dipole1): $\vec{E}_2(\vec{r}_1) = \frac{1}{4 \pi \varepsilon_0} \frac{1}{r^3} \left( 3 \vec{p}_2 \cdot \hat{r}_1 \right) \hat{r}_1 - \vec{p}_2$

$\vec{r}_2 = -\vec{r}_1 = -\vec{r}$

$\vec{E}_1$-field of dipole1 (@ dipole2): $\vec{E}_1(\vec{r}_2) = \frac{1}{4 \pi \varepsilon_0} \frac{1}{r^3} \left( 3 \vec{p}_1 \cdot \hat{r}_2 \right) \hat{r}_2 - \vec{p}_1$

$\vec{r}_1 \equiv \vec{r}$

Notice that: $W_{\min}$ occurs when $\vec{p}_1$ is anti-parallel to $\vec{p}_2$, i.e. when $\vec{p}_2 = -\vec{p}_1$ and when: $\vec{p}_1, \vec{p}_2 \perp \hat{r}$ (or anti - $\perp$ to $\hat{r}$) then $\vec{p}_1 \cdot \hat{r} = 0$ and $\vec{p}_2 \cdot \hat{r} = 0$. 

\begin{align*}
W_{p_1,p_2} &= P.E. = -\vec{p}_1 \cdot \vec{E}_2(\vec{r}_1) - \vec{p}_2 \cdot \vec{E}_1(\vec{r}_2) \\
&= -\frac{1}{4 \pi \varepsilon_0} \left( \frac{1}{r^3} \right) \left[ (3 \vec{p}_2 \cdot \hat{r}_1) (\vec{p}_1 \cdot \hat{r}_1) - \vec{p}_1 \cdot \vec{p}_2 \right] - \frac{1}{4 \pi \varepsilon_0} \left( \frac{1}{r^3} \right) \left[ (3 \vec{p}_1 \cdot \hat{r}_2) (\vec{p}_2 \cdot \hat{r}_2) - \vec{p}_1 \cdot \vec{p}_2 \right]
\end{align*}

Now: $\vec{r} \equiv \vec{r}_1 = -\vec{r}_2$ and $\vec{p}_1 \cdot \vec{p}_2 = \vec{p}_2 \cdot \vec{p}_1$

$$W = P.E. = -\frac{1}{4 \pi \varepsilon_0} \left( \frac{1}{r^3} \right) \left[ (3 \vec{p}_2 \cdot \hat{r}) (\vec{p}_1 \cdot \hat{r}) - \vec{p}_1 \cdot \vec{p}_2 \right] + \frac{1}{4 \pi \varepsilon_0} \left( \frac{1}{r^3} \right) \left[ (3 \vec{p}_1 \cdot \hat{r}) (\vec{p}_2 \cdot \hat{r}) - \vec{p}_1 \cdot \vec{p}_2 \right]$$

Then:

$$W = -\frac{2}{4 \pi \varepsilon_0} \left( \frac{1}{r^3} \right) \left[ 3 (\vec{p}_1 \cdot \hat{r}) (\vec{p}_2 \cdot \hat{r}) - \vec{p}_1 \cdot \vec{p}_2 \right]$$

Notice that: $W_{\min} / P.E._{\min}$ occurs when $\vec{p}_1$ is anti-parallel to $\vec{p}_2$, i.e. when $\vec{p}_2 = -\vec{p}_1$
So let’s put in some actual numbers:

\[
\varepsilon_o = 8.85 \times 10^{-12} \frac{C^2}{N \cdot m^2} \left( \equiv \frac{F}{m} \right)
\]

A typical intermolecular separation distance for the water (H₂O) molecule is

\[
\left\langle r_{H_2O-H_2O} \right\rangle \sim 10 \AA = 10 \times 10^{-10} \text{ m} = 1 \text{ nm}
\]

\[
p_1 = p_2 = p_{H_2O} = 6.1 \times 10^{-30} \text{ Coulomb-meters}
\]

\[
W_{\min}^{p_{H_2O}} \left/ P.E._{\min}^{p_{H_2O}} \right. \approx - \frac{1}{2\pi \varepsilon_o \times 8.85 \times 10^{-12}} \frac{1}{(10^{-9})^3} (6.1 \times 10^{-30})^2 = 6.69 \times 10^{-22} \text{ Joules}
\]

⇒ Very small energy!!!

Now liquid water (room temperature \( T = 300K \)) also has thermal energy associated with it.

Boltzmann Kinetic Theory: – get a contribution to thermal energy of \( \frac{1}{2} k_B T \) for

a.) each kinetic degree of freedom
b.) each rotational degree of freedom
c.) each vibrational degree of freedom

\[
k_B = \text{Boltzmann’s Constant} = 1.38 \times 10^{-23} \text{ Joules/K}
\]

For water (H₂O) @ \( T = 300K \):

a.) kinetic: \( v_x, v_y, v_z \Rightarrow \frac{3}{2} k_B T \)

b.) rotational: \( I_x, I_y \Rightarrow \frac{2}{2} k_B T \)

c.) vibrational: none \( \Rightarrow 0 \) (i.e. no quantum vibrations of water molecule H₂O

no H-O-H vibrational excitations @ \( T = 300K \))

Thus, for a single H₂O molecule: \( W_{thermal}^{H_2O} = \frac{5}{2} k_B T \).

Since we’re considering two H₂O molecules (here), then (using superposition principle):

\[
W_{thermal}^{H_2O} (TOT) = 2W_{thermal}^{H_2O} = 5k_B T = 5 \times 1.38 \times 10^{-23} \times 300 = 2.07 \times 10^{-20} \text{ Joules}
\]

\[
W_{thermal}^{H_2O} (TOT) = 2.07 \times 10^{-20} \text{ Joules} \gg \left| W_{\min}^{p_{H_2O}} \right| = 6.69 \times 10^{-22} \text{ Joules}
\]

Ratio: \( W_{H_2O}^{thermal} (TOT) \left/ \left| W_{min}^{p_{H_2O}} \right| \right. = 30.9 \)

Sum: \( W_{TOT}^{H_2O} = W_{thermal}^{H_2O} + W_{min}^{p_{H_2O}} = 2.07 \times 10^{-20} J - 6.69 \times 10^{-22} J = 2.00 \times 10^{-20} \text{ Joules} \)
Thus, we see that the internal energy of water (@ the microscopic level) is dominated by thermal energy at $T = 300K$ (room temperature). In order for the dipole-dipole term $W_{min}^{p_1p_2}$ to actually dominate, the water temperature would have to be $T_{H_2O} \leq 9.7K$ for $W_{min}^{p_1p_2}$ to dominate $W_{TOT}^{H_2O} \leq 0$.

So, typically (but not always) for polar materials (gases / liquids / solids), macroscopic amounts of individual molecules ($\approx N_A = 6 \times 10^{23}$ molecules/mol) the thermal energies overwhelm the dipole-dipole interaction energies at room temperature.

No net macroscopic alignment of permanent microscopic electric dipoles occurs at $T = 300K$. When one places either non-polar or polar materials (at $T = 300K$) in externally applied electric field $\vec{E}_{ext}$, nevertheless, there is a net, partial macroscopic alignment of either induced microscopic electric dipole moments (for non-polar materials) or permanent electric dipole moments (for polar materials).

A “snapshot” of a dielectric material: (with either induced atomic / molecular electric dipole moments or permanent electric dipole moments at $T = 300K$)

- **No external applied field $\vec{E}_{ext} = 0$**
- **With external applied field $\vec{E}_{ext} \neq 0$**

Random orientation(s) of induced / permanent electric dipole moments at microscopic scale - atomic or molecular at $T = 300K$.

Partial alignment of induced / permanent electric dipole moments at microscopic scale – atomic or molecular at $T = 300K$ – when remove $\vec{E}_{ext}$, alignment rapidly disappears.

Both pictures change from one instant to the next:
- Thermal fluctuations (fluctuations in thermal energy density)
- Quanta of thermal energy ($EM$ energy – virtual photons) “traded” between constituents (atoms / molecules) at microscopic scale.
Electric Dipole Moment Per Unit Volume of Material (a.k.a. Electric Polarization) $\vec{P}(\vec{r})$

For a single atom (or molecule or physical dipole), we have seen that the electric dipole moment of the charge distribution is given by: $\vec{p}(\vec{r}) = \int_{\text{vol}} v \rho(\vec{r}')d\vec{r}'$

For atoms / molecules, the integration volume $\text{vol}'$ is associated with the space “occupied” by that atom / molecule, but it essentially can be over all space.

For a macroscopic sample of matter (gas, liquid or solid consisting of many, many atoms, molecules (i.e. a sample containing $N_A \sim O(10^{23})$ molecules) it makes sense that we can define a quantity / parameter known as the electric dipole moment per unit volume (also known as the electric polarization) $\vec{P}(\vec{r})$:

Electric Dipole Moment Per Unit Volume (a.k.a. Electric Polarization):

$$\vec{P}(\vec{r}) = \frac{\sum_{i=1}^{N} \vec{p}_\text{vol}_i (\vec{r}_i)}{\text{Volume Element } d\tau} = \frac{\sum_{i=1}^{N} Q_i \vec{d}_\text{vol}_i (\vec{r}_i)}{\text{Volume Element } d\tau}$$

Where the infinitesimal volume element $d\tau$ is centered on the vector $\vec{r}$, and the $\vec{r}_i$ vectors associated with each atom/molecule are contained within the infinitesimal volume element $d\tau$.

Thus: $\vec{r} = \frac{1}{N} \sum_{i=1}^{N} \vec{r}_i$.

Note that the physical interpretation of $\vec{P}(\vec{r})$ is that it is the macroscopic average of the microscopically-summed-over electric dipole moment per unit volume. Important!!!

What are the S.I. units of the electric polarization, $\vec{P}(\vec{r})$? From above, we see that they are:

$$\frac{Q \cdot \text{length}}{(\text{length})^3} = \frac{Q}{\text{length}^2} \Rightarrow \text{Coulombs / meter}^2$$

Thus, $\vec{P}(\vec{r})$ has the same S.I. units as surface charge density, $\sigma$!

Note that if macroscopic dielectric / insulating material has no net electric charge associated with it, i.e. $dQ(\vec{r}) = \sum_{i=1}^{N} Q_i(\vec{r}_i) = 0$ in each of the infinitesimal volume elements, $d\tau$ centered on the vector $\vec{r}$, then the monopole moment $M_0$ of the charge distribution associated with the entire dielectric material, integrating over the whole volume: $M_0 = Q_{\text{tot}} = \int_{\text{vol}} dQ(\vec{r}) = \int_{\text{vol}} \rho(\vec{r}')d\tau' = 0$. 

©Professor Steven Errede, Department of Physics, University of Illinois at Urbana-Champaign, Illinois 2005 - 2008. All rights reserved.
Thus, any potential \( V(\vec{r}) \) that arises due to (microscopic, and thus macroscopic) polarization of the dielectric material will be due to the next most important term in the multipole expansion of the potential, namely the (macroscopic) electric dipole moment associated with that material!

We already know the potential \( V_{\text{dipole}}(\vec{r}) \) (and corresponding \( \vec{E}_{\text{dipole}}(\vec{r}) = -\nabla V_{\text{dipole}}(\vec{r}) \)) associated with a single, microscopic pure electric dipole moment \( \vec{p} \) is:

\[
V_{\text{dipole}}(\vec{r}) = \frac{1}{4\pi\varepsilon_0} \left( \frac{\vec{p} \cdot \vec{r}}{r^2} \right)
\]

The electric dipole moment \( p(\vec{r}') \) is located at the source point \( \vec{r}' \)

For a macroscopic dielectric material, an infinitesimal volume element \( d\tau' \) has a net electric dipole moment \( \vec{p}(\vec{r}') \) associated with it of:

\[
\vec{p}(\vec{r}') = \vec{P}(\vec{r}') d\tau'
\]

(i.e. \( \vec{P}(\vec{r}') \equiv \frac{\vec{p}(\vec{r}')}{d\tau'} \))

The infinitesimal contribution to the potential \( dV_{\text{dipole}}(\vec{r}) \) due to this \( \vec{p}(\vec{r}') = \vec{P}(\vec{r}') d\tau' \) is thus:

\[
dV_{\text{dipole}}(\vec{r}) = \frac{1}{4\pi\varepsilon_0} \left( \frac{\vec{P}(\vec{r}') \cdot \vec{r}}{r^2} \right) = \frac{1}{4\pi\varepsilon_0} \left( \frac{\vec{P}(\vec{r}') \cdot \vec{r}}{r^2} \right) d\tau'
\]

Then integrating this expression over the volume \( v' \) of the dielectric material, we have:

\[
V_{\text{dipole}}(\vec{r}) = \int_{v'} dV_{\text{dipole}}(\vec{r}) = \frac{1}{4\pi\varepsilon_0} \int_{v'} \left( \frac{\vec{P}(\vec{r}') \cdot \vec{r}}{r^2} \right) d\tau' \equiv \text{Macroscopic potential due to a polarized dielectric material}
\]

Now:

\[
\vec{V}'\left( \frac{1}{r} \right) = \vec{V}'\left( \frac{1}{r - \vec{r}'} \right) \quad \Rightarrow \quad \text{n.b. } \vec{V}' \text{ refers to differentiation with respect to source coordinates only!!!}
\]

\[
\vec{V}'\left( \frac{\vec{r}}{r^2} \right) = \frac{\vec{r} - \vec{r}'}{r^2 - |\vec{r} - \vec{r}'|^2}
\]

\[
\vec{V}'\left( \frac{\vec{r}}{r^3} \right) = \frac{\vec{r} - \vec{r}'}{|\vec{r} - \vec{r}'|^3}
\]
Thus, using \( \vec{V} \left( \frac{1}{r} \right) = \frac{\vec{r}}{r^2} \) we can write \( V_{\text{dipole}} (\vec{r}) = \frac{1}{4\pi\varepsilon_o} \int_v \left( \frac{\vec{P}(\vec{r}') \cdot \vec{r}}{r^2} \right) d\tau' \) as:

\[
V_{\text{dipole}} (\vec{r}) = \frac{1}{4\pi\varepsilon_o} \int_v \vec{P}(\vec{r}') \vec{\nabla}' \left( \frac{1}{r} \right) d\tau'
\]

{n.b. In practice, it is often extremely difficult to explicitly carry out this integration, except for a few cases with very simple geometry and / or simple polarization(s), e.g. \( \vec{P}(\vec{r}') = \text{constant} \).

Note that in general that \( \vec{P}(\vec{r}') \) (= electric dipole moment per unit volume / a.k.a. electric polarization) is never known \textit{a-priori} (i.e. before the fact), but is instead inferred \textit{a-posteriori} (i.e. after the fact) from known, physically measurable quantities / parameters.

How is this accomplished???

Note that:
\[
\vec{V} \cdot \vec{f} \vec{A} = \vec{f} \vec{V} \cdot \vec{A} + \frac{1}{A} \vec{V} \vec{f} 
\]
Then:
\[
\vec{A} \vec{V} f = \vec{V} \vec{f} A - \vec{f} \vec{V} \vec{A}
\]

Let:

\[
f = \frac{1}{r} = \frac{1}{|\vec{r} - \vec{r}'|} \quad \text{and} \quad \vec{A} \equiv \vec{P}
\]

Then:

\[
V_{\text{dipole}} (\vec{r}) = \frac{1}{4\pi\varepsilon_o} \int_v \vec{P}(\vec{r}') \vec{\nabla}' \left( \frac{1}{r} \right) d\tau' = \frac{1}{4\pi\varepsilon_o} \int_v \vec{\nabla}' \left( \frac{\vec{P}(\vec{r}')}{r} \right) d\tau' - \frac{1}{4\pi\varepsilon_o} \int_v \left( \frac{1}{r} \right) (\vec{V}' \cdot \vec{P}(\vec{r}')) d\tau'
\]

Thus:

\[
V_{\text{dipole}} (\vec{r}) = \frac{1}{4\pi\varepsilon_o} \oint_S \left( \frac{1}{r} \right) \vec{P}(\vec{r}') \vec{n}' dA' - \frac{1}{4\pi\varepsilon_o} \int_v \left( \frac{1}{r} \right) (\vec{V}' \cdot \vec{P}(\vec{r}')) d\tau'
\]

= Potential due to (bound) surface charge density

\[
\sigma_b (\vec{r}') \equiv \vec{P}(\vec{r}') \vec{n}'
\]
(SI units: Coulombs/m²)

= Potential due to (bound) volume charge density

\[
\rho_b (\vec{r}') \equiv -\vec{V}' \cdot \vec{P}(\vec{r}')
\]
(SI units: Coulombs/m³)

\( \vec{n}' = \text{Outward-pointing unit normal vector on bounding surface } S' \).

The bound surface charge density \( \sigma_b (\vec{r}') \equiv \vec{P}(\vec{r}') \vec{n}' \) and bound volume charge density \( \rho_b (\vec{r}') \equiv -\vec{V}' \cdot \vec{P}(\vec{r}') \) are called \textit{bound} charge densities because these charges cannot move – they are certainly not \textit{free} charges – because they are \textit{bound} to atoms / molecules.
Then, using these two relations, 
\[
\sigma_B(\vec{r}') \equiv \vec{P}(\vec{r}') \cdot \hat{n}
\]
and 
\[
\rho_B(\vec{r}') \equiv -\vec{\nabla} \cdot \vec{P}(\vec{r}')
\]
we see that:

\[
V_{\text{dipole}} (\vec{r}) = \frac{1}{4\pi \varepsilon_0} \int_S \left( \frac{1}{r} \right) \vec{P}(\vec{r}') \cdot d\vec{A}' - \frac{1}{4\pi \varepsilon_0} \int_V \left( \frac{1}{r} \right) \left( \vec{\nabla} \cdot \vec{P}(\vec{r}') \right) d\tau'
\]

\[
= \frac{1}{4\pi \varepsilon_0} \int_S \left( \frac{\sigma_B(\vec{r}')}{r} \right) d\vec{A}' + \frac{1}{4\pi \varepsilon_0} \int_V \left( \frac{\rho_B(\vec{r}')}{r} \right) d\tau'
\]

Physically what this formula / above expression says is that the electric potential \(V_{\text{dipole}} (\vec{r})\) and hence \(E\)-field \(\vec{E}_{\text{dipole}} (\vec{r}) = -\vec{\nabla} V_{\text{dipole}} (\vec{r})\) due to the macroscopic electric polarization \(\vec{P}(\vec{r}')\) of dielectric material is formally / mathematically equivalent to that of a potential associated with a bound surface charge density \(\sigma_B(\vec{r}') = \vec{P}(\vec{r}') \cdot \hat{n}'\) plus a contribution to the potential associated with a bound volume charge density \(\rho_B(\vec{r}') = -\vec{\nabla} \cdot \vec{P}(\vec{r}')\)

So instead of having to integrate over contributions from infinitesimal-sized point-like atomic / molecular dipoles contained within the volume \(V'\) of the dielectric material, we simply find / determine the bound charge densities \(\sigma_B\) and \(\rho_B\), and then calculate \(V(\vec{r})\) and \(\vec{E}(\vec{r})\) the same exact way(s) we have already done e.g. for the \textit{free} charge densities \(\sigma_f\) and \(\rho_f\) !!

Consider an infinitesimal, single volume element \(d\tau'(\vec{r}')\) inside e.g. a \textit{uniformly} polarized block of dielectric material - i.e. a dielectric with uniform / constant polarization \(\vec{P}(\vec{r}') = P_o \hat{x}\) e.g. a block of dielectric material (such as plastic) inserted between the plates of a parallel plate capacitor:

\[
\text{n.b: The number density of molecules is } n_{mol} = \# \text{ molecules/unit volume (i.e. } \# \text{ molecules/m}^3)\]
Suppose the mean charge displacement, i.e. \( <\text{charge displacement}> \) of molecules, going from an unpolarized state “\( \bigcirc \)” to a polarized state, e.g. “\( \bigotimes \)” is an average distance of \( \hat{d} = d\hat{x} \).

Then the (average/mean) amount of charge displaced in a volume element \( d\tau' \) is (see above figure on previous page) is:

\[
dQ = n_{\text{mol}} Qd\tau' = n_{\text{mol}} Q\hat{d}\cdot d\hat{S}'\quad \text{where: } d\hat{S}' = \hat{n}'dS' \iff d\hat{S} = \hat{n}dS \\
\]

\[
dQ = n_{\text{mol}} Q\hat{d}\cdot \hat{n}'dS' \quad \text{and: } n_{\text{mol}} = \# \text{ molecules/m}^3
\]

\( dQ \) = the amount of charge displaced in the polarization process, crossing an area element \( dS' \).

Now we re-arrange / rewrite this a bit:

Since: \( \bar{\rho} = Q\hat{d} = \text{average/mean} \) electric dipole moment per molecule in the volume element \( d\tau' \).

Then: \( dQ = n_{\text{mol}} \bar{\rho}d\tau' \cdot \hat{n}'dS' = n_{\text{mol}} \bar{\rho} \cdot \hat{n}'dS' \)

But: \( n_{\text{mol}} \bar{\rho}(\vec{r}') \equiv \bar{\rho}(\vec{r}') \) \{Since the electric polarization, \( \bar{\rho}(\vec{r}') \) is defined as the (macroscopic) electric dipole moment per unit volume!!!\}

i.e.: \( \bar{\rho}(\vec{r}') \equiv n_{\text{mol}} \bar{\rho}(\vec{r}') \) where \( n_{\text{mol}} = \# \text{ molecules/unit volume} \)

and \( \bar{\rho}(\vec{r}') = \text{electric dipole moment per molecule, in volume element } d\tau' \)

\{Check units/dimensions of \( \bar{\rho}(\vec{r}') \equiv n_{\text{mol}} \bar{\rho}(\vec{r}') = (\#/\text{m}^3 \ast \text{Coulomb-m} = \text{Coulombs}/\text{m}^2 \text{ – Yes!!})\}

Thus we see that:

\[
dQ = n_{\text{mol}} \bar{\rho}(\vec{r}') \cdot \hat{n}'dS' = n_{\text{mol}} \bar{\rho}(\vec{r}') \cdot \hat{n}'dS' = \bar{\rho}(\vec{r}') \cdot \hat{n}'dS' = dQ_B
\]

= bound charge \( Q_B \) on the surface area \( dS' \) of one side of the infinitesimal volume element \( d\tau' \).

If we now integrate \( dQ_B = \bar{\rho}(\vec{r}') \cdot \hat{n}'dS' \) (= amount of charge displaced in the polarization process) over all 6 surfaces of the infinitesimal volume element \( d\tau' \) (for simplicity, assume \( d\tau' \) to be a cube of side \( dS' \)), and for again for simplicity’s sake, let us assume that the electric polarization, \( \bar{\rho}(\vec{r}') \) has negligible variation (i.e. is a constant) over the infinitesimal volume element, \( d\tau' \) such that e.g. \( \bar{\rho}(\vec{r}') = \bar{P}_o \cdot \hat{x} \).

Then:

\[
Q^\text{net} \quad \text{(of } \vec{d} \tau' \text{ at } \vec{r}') = \bar{P}(\vec{r}') \cdot \hat{n}_1dS' + \bar{P}(\vec{r}') \cdot \hat{n}_2dS' + \bar{P}(\vec{r}') \cdot \hat{n}_3dS' \\
+ \bar{P}(\vec{r}') \cdot \hat{n}_4dS' + \bar{P}(\vec{r}') \cdot \hat{n}_5dS' + \bar{P}(\vec{r}') \cdot \hat{n}_6dS'
\]

where: \( \hat{n}_1 = -\hat{n}_4 = \hat{x} \) and \( \hat{n}_2 = -\hat{n}_5 = \hat{y} \) and \( \hat{n}_3 = -\hat{n}_6 = \hat{z} \).
Then if: \( \bar{P}(\vec{r}') = P_o \hat{x}, \) and

\[
Q_{B}'(\vec{r}') = \bar{P}(\vec{r}') \cdot \hat{n}_i dS' + \bar{P}(\vec{r}') \cdot \hat{n}_j dS' + \bar{P}(\vec{r}') \cdot \hat{n}_k dS'
\]

\[
= P_o dS' (\hat{x} \cdot \hat{x} + \hat{y} \cdot \hat{y} + \hat{z} \cdot \hat{z}) = 0
\]

Thus we see {here} that the net charge displacement across the entire surface \( S' \) enclosing the infinitesimal volume element, \( d\tau' \) is \( Q_{B}' = 0 \), because \( Q_1 = -Q_2 \) and \( Q_3 = Q_5 = Q_6 = 0 \).

(Not that this is true only for the case of uniform/constant polarization, \( \bar{P} \) throughout \( d\tau' \) i.e. in general, \( Q_{B}' = 0 \) for arbitrary polarization \( \bar{P} \) throughout \( d\tau' \).)

If \( \bar{P}(\vec{r}') = P_o \hat{x}, \) then (obviously) the bound volume charge density \( \rho_B'(\vec{r}') = -\vec{\nabla}' \cdot \bar{P}(\vec{r}') = 0 \)

because: \( \rho_B'(\vec{r}') = -\vec{\nabla}' \cdot \bar{P}(\vec{r}') = -\vec{\nabla}' \cdot P_o \hat{x} = -P_o (\vec{\nabla}' \cdot \hat{x}) = 0. \)

n.b. This result also holds for macroscopic volumes: \( Q_B = \oint_{S'} \bar{P}(\vec{r}') \cdot d\vec{A}' \)

i.e. there will be no bound volume charge density, \( \rho_B'(\vec{r}') = 0 \) if the electric polarization (electric dipole moment per unit volume) \( \bar{P}(\vec{r}') \) is uniform / constant, e.g. \( \bar{P}(\vec{r}') = P_o \hat{x} \)

throughout the macroscopic dielectric medium.

If \( \bar{P}(\vec{r}') \) is not uniform in the macroscopic volume \( v' \),

then: \( Q_B = \oint_{S'} \bar{P}(\vec{r}') \cdot d\vec{A}' = \oint_{S'} \bar{P}(\vec{r}') \cdot \hat{n}' d\vec{A}' \neq 0 \)

Note that if \( dQ(\vec{r}') = \bar{P}(\vec{r}') \cdot \hat{n}' dS' \neq 0 \) exists on the entire/total surface \( dS' \) associated with a volume element \( d\tau' \) then this is also = to the net charge that flows out of (or into) the infinitesimal volume element \( d\tau' \) across/through the total surface area element \( dS' \) when the dielectric material is polarized.

\[ \Rightarrow \text{Then a net charge } -dQ_B \text{ must remain in the infinitesimal volume } d\tau', \text{ so then:} \]

\[
\int_{\gamma} \rho_B(\vec{r}') d\tau' = -Q_B = -\oint_{S'} \bar{P}(\vec{r}') \cdot d\vec{A}' = -\int_{\gamma} (\vec{\nabla}' \cdot \bar{P}(\vec{r}')) d\tau' \Rightarrow \rho_B'(\vec{r}') = -\vec{\nabla}' \cdot \bar{P}(\vec{r}')
\]

Thus, we see that \( \sigma_B \) and \( \rho_B \) are (bound / induced / polarization) surface and volume charge densities, respectively.

Synonyms of each other here
**More on the Physical Interpretation of the Bound Charges:**

We have seen that $\sigma_B$ and $\rho_B$ represent real, physical accumulations of electric charges on the surfaces and/or in the volume of dielectric materials, respectively.

However, the primary distinction associated with these two physical quantities is that $Q_B = \oint_S \sigma_B dA'$ and $Q_B = \int_v \rho_B d\tau'$ are associated with bound charges – i.e. charges that are bound to atoms / molecules – they are *not* free surface / volume charge densities.

c.f. bound charges $\sigma_B$ and $\rho_B$ with free charges $\sigma_{free}$ and $\rho_{free}$ (which *can* move freely on bounding surfaces ($S'$) and volumes ($v'$))

Consider a fully-polarized, very long dielectric rod of radius $R$ with uniform polarization $\vec{P} = P_o \hat{z}$  $\parallel$ to the $\hat{z}$ -axis of the polarized dielectric rod:

Carefully cut out a very thin disk e.g. of thickness $d = 10\AA = 10^{-9} m$

The thin disk has cross-sectional area $A = \pi R^2$:

We can replace the polarization, $\vec{P}$ by bound surface charges $Q_{B-}$ and $Q_{B+}$! Thus, the thin disk has (macroscopic) electric dipole moment $\vec{p} = Q_{B} d \hat{z}$

However, the macroscopic electric dipole moment of the disk is also:

$\vec{p} = \vec{P} \text{Volume of disk} = \vec{P} * (Ad) = \vec{P} (\pi R^2 d) = P_o (\pi R^2 d) \hat{z} = Q_{B} d \hat{z}$

(Since the macroscopic polarization $\vec{P} = \text{macroscopic electric dipole moment per unit volume}!!!)

Therefore: $P_o (\pi R^2 d) = Q_{B} d$ or: $Q_{B} = P_o \pi R^2 = P_o A$

Or: $\sigma_{B+} = \frac{Q_{B+}}{A}$ $\Rightarrow$ $Q_{B+} = \sigma_{B+} A = (\vec{P} \cdot \hat{n}_1) A = P_o \hat{z} \cdot (\hat{+z}) \cdot A = + P_o A$ where: $\hat{n}_1 = + \hat{z}$

$\sigma_{B-} = \frac{Q_{B-}}{A}$ $\Rightarrow$ $Q_{B-} = \sigma_{B-} A = (\vec{P} \cdot \hat{n}_2) A = P_o \hat{z} \cdot (-\hat{z}) \cdot A = - P_o A$ and: $\hat{n}_2 = - \hat{z}$

But: $\sigma_B = \vec{P} \cdot \hat{n}$

Thus we see that: $Q_{B+} = -Q_{B-} = P_o A$ and: $\sigma_{B+} = -\sigma_{B-} = \frac{Q_{B+}}{A} = -\frac{Q_{B-}}{A} = P_o$
If we instead make an oblique cut in the long, polarized rod:

\[
A_{end}^{\text{oblique}} = A / \cos \theta
\]

cross-sectional area \( A = \pi R^2 \)

\[
\sigma_{B+}^{\text{oblique}} (\hat{n}) = \hat{P} \cdot \hat{n} = P_o \hat{z} \cdot \hat{n} = P_o \cos \theta
\]

\[
Q_{B+}^{\text{oblique}} (\hat{n}) = \sigma_{B+}^{\text{oblique}} (\hat{n}) A_{end}^{\text{oblique}} = (P_o \cos \theta) \left( A / \cos \theta \right) = P_o A = \text{same result!}
\]

If the polarization is non-uniform, then \( \exists \) accumulations of bound charge within the polarized dielectric material as well as on the surface of the dielectric material.

**Diverging Polarization** \( \hat{P}(\vec{r}) \):

\[
\sigma_{B+}(\vec{r} = R) = \hat{P}(\vec{r}) \cdot \hat{n} \bigg|_{r=R} = \hat{P}(\vec{r}) \cdot \hat{r} \bigg|_{r=R}
\]

\[
Q_{B+} = \sigma_{B+} A_{\text{sphere}} = 4\pi R^2 \sigma_{B+}
\]

We know by charge conservation that:

\[
Q_{B-} = -Q_{B+} = -4\pi R^2 \sigma_{B+}
\]

\[
Q_{B+} = \int_{\Omega} \rho_B (\vec{r'}) d\tau' = \int_{\Omega'} \nabla' \cdot \hat{P} (\vec{r'}) d\tau'
\]

**Griffiths Example 4.2:**

Determine the electric field associated with uniformly polarized sphere of radius \( R \)

\[
\hat{P} = P_o \hat{z} = \text{constant}
\]

Here:

Volume bound charge density: \( \rho_B(\vec{r}) = -\nabla \cdot \hat{P}(\vec{r}) = -\nabla \cdot P_o \hat{z} = 0 \)

Surface bound charge density: \( \sigma_B(r = R) = \hat{P}(\vec{r}) \cdot \hat{n} \bigg|_{r=R} = P_o \hat{z} \cdot \hat{r} = P_o \cos \theta \quad \hat{z} \cdot \hat{r} = \cos \theta \)
In Griffiths Example 3.9 we obtained for \( \sigma = k \cos \theta \) on a sphere of radius \( R \) that for \( k = P_o \):

\[
V(r) = \begin{cases} 
\frac{P_o}{3\varepsilon_o} r \cos \theta & (r \leq R) \\
\frac{P_o}{3\varepsilon_o} \left( \frac{R^3}{r^2} \right) \cos \theta & (r \geq R)
\end{cases}
\]

Now \( z = r \cos \theta \), and inside the sphere \( (r \leq R) \), the electric field intensity is:

\[
\vec{E}_{\text{inside}}(r \leq R) = -\nabla V(r \leq R) = -\frac{\vec{P}}{3\varepsilon_o} = -\frac{P_o}{3\varepsilon_o} \hat{\mathbf{z}} \text{ for } r \leq R
\]

Note that outside the sphere \( (r \geq R) \), the potential \( V(r \geq R) \) is identical to that of a point electric dipole at the origin!

\[
\vec{p} = \vec{P} \ast \text{Volume of sphere} = \frac{4}{3} \pi R^3 \vec{P} = \frac{4}{3} \pi R^3 P_o \hat{\mathbf{z}}
\]

Electric dipole moment per unit volume

\[
V(r \geq R) = \frac{P_o}{3\varepsilon_o} \left( \frac{R^3}{r^2} \right) \cos \theta = \frac{1}{4\pi\varepsilon_o} \frac{4 \pi R^3}{3 r^2} P_o (\hat{\mathbf{z}} \ast \vec{r}) = -\frac{1}{4\pi\varepsilon_o} \left( \frac{\vec{p} \ast \vec{r}}{r^2} \right)
\]

Then use \( \vec{E}_{\text{outside}}(r \geq R) = -\nabla V(r \geq R) \) to obtain electric dipole field intensity outside the sphere (see P435 Lecture Notes 8).

Lines of \( \vec{E}_{\text{outside}}(r \geq R) \) and \( \vec{E}_{\text{inside}} = -\frac{1}{3\varepsilon_o} P_o \hat{\mathbf{z}} \):

Note the discontinuity in the normal component of \( \vec{E} @ r = R \)!!
This is due to the existence of surface bound charge density \( \sigma_B \) on surface of the sphere!!
The Polarization Current Density $\vec{J}_B$

Suppose we have an initially un-polarized dielectric, which we then place in an external electric field $\vec{E}_{ext}$ – but one which varies extremely slowly with time. Then the (induced) polarization $\vec{P}$ in the dielectric will also vary extremely slowly with time, simply tracking the externally-applied electric field.

Using electric charge conservation (i.e. the using the empirical fact that electric charge cannot be created, nor can it be destroyed), we obtain the so-called continuity equation for bound charge in a dielectric, which we simply give here (for now – we will discuss in more detail, in the future):

$$\int_{S'} \vec{J}_B(\vec{r'}) \cdot d\vec{A}' = -\frac{\partial}{\partial t} \int_{v'} \rho_B(\vec{r'}) \, d\tau'$$

Using the divergence theorem and $\vec{B} \cdot \vec{J} = -\nabla \cdot \vec{P}$ we obtain:

$$\int_{v'} \vec{v}' \cdot \vec{J}_B(\vec{r'}, t) \, d\tau' = -\frac{\partial}{\partial t} \int_{v'} \rho_B(\vec{r'}) \, d\tau' = +\frac{\partial}{\partial t} \int_{v'} \vec{v}' \cdot \vec{P}(\vec{r'}, t) \, d\tau' = \int_{v'} \vec{v}' \cdot \frac{\partial \vec{P}(\vec{r'}, t)}{\partial t} \, d\tau'$$

The above volume integral equation must be valid for arbitrary volumes, $v'$ (e.g. for $\approx$ a few molecules in the dielectric $\rightarrow$ entire dielectric). Therefore the integrands in the volume integrals must be equal to each other at each/every point in space, and at each/every instant in time:

$$\vec{J}_B(\vec{r'}, t) = \frac{\partial \vec{P}(\vec{r'}, t)}{\partial t} \quad \Leftarrow \text{Continuity equation for bound electric charge}$$

SI units of Polarization Current Density, $J_B = \frac{\partial \vec{P}}{\partial t} = \text{Coulombs/m}^2\text{-sec} = \text{Amperes/m}^2$

(1 Ampere of current $\equiv$ 1 Coulomb / second of charge passing through a $\perp$ imaginary plane)