L5 Polarizability

Lecture outline:
• Polarizability of molecules.
• The dielectric constant.

L5.1 Polarizability

The polarizability of molecules.
Molecules without intrinsic dipole moment (non-polar).
Electronic polarizability - electrons move in response to field:

Then always \( \mathbf{p} = \alpha \mathbf{E} \), where \( \alpha \) is the polarizability.
L5.2 Polarizability

Estimate $\alpha$ for H atom. Electron cloud radius is $a \approx 10^{-10}$ m.

Assume the electron charge is uniformly spread in the cloud.

E at the nucleus: $E \times 4\pi d^2 = \frac{\text{charge enclosed}}{\varepsilon_0} = \frac{d^3 e}{a^3 \varepsilon_0}$

$$E = \frac{d^3 e}{\varepsilon_0 a^3 4\pi d^2} = \frac{d e}{4\pi \varepsilon_0 a^3} = \frac{p}{4\pi \varepsilon_0 a^3}$$

so $p = 4\pi \varepsilon_0 a^3 E$

and $\alpha = 4\pi \varepsilon_0 a^3 \approx 4\pi \varepsilon_0 \times 10^{-30} m^3$

L5.3 Polarizability

<table>
<thead>
<tr>
<th>$\frac{\alpha}{4\pi \varepsilon_0}$ (measured)</th>
<th>Table of $\alpha/4\pi \varepsilon_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$ in $m^3$</td>
<td>H $0.66 \times 10^{-30}$ (tightly bound electrons)</td>
</tr>
<tr>
<td></td>
<td>He $0.21 \times 10^{-30}$ (loosely bound electrons)</td>
</tr>
<tr>
<td></td>
<td>Li $12 \times 10^{-30}$ (loosely bound electrons)</td>
</tr>
<tr>
<td></td>
<td>CH$_4$ $2.6 \times 10^{-30}$</td>
</tr>
<tr>
<td></td>
<td>CO$_2$ $4.05 \times 10^{-30}$, if $E$ is along axis</td>
</tr>
<tr>
<td></td>
<td>1.8 $\times 10^{-30}$, if $E$ is $\perp$ axis</td>
</tr>
</tbody>
</table>

If we simply added up $\alpha$'s for 1 C and 4 Hs, we would get $4.1 \times 10^{-30}$. The binding of the atoms into a molecule has changed the electronic structure. A useful clue for chemists.

Electrons can move further along axis

$\alpha$ is no longer a simple constant of proportionality, it is a tensor.
L5.4 Polarizability

Relation of Polarizability to the Dielectric Constant:

We have

\[ p = \alpha E, \quad P = np \]

Dipole moment  Polarization  Number/volume

So it looks like

\[ P = n\alpha E = (K - 1)\varepsilon_0 E \]

and

\[ \alpha = \frac{\varepsilon_0}{n} (K - 1) \]

But

\[ p = \alpha E_{other} \quad E_{other} \text{ is field imposed from outside} \]

and

\[ P = (K - 1)\varepsilon_0 E \quad E \text{ is field inside the material} \]

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L5.5 Polarizability

These \( E \)s are not the same unless material is very dilute, like a gas.

Consider a dielectric with \( P \) and \( E \) inside it.

\( E \) is the sum of the outside field \( (E_{other}) \) and the field produced by the dielectric \( (E_{self}) \):

\[ E = E_{other} + E_{self} \]

Take a cavity:
L5.6 Polarizability

\[ E \text{ inside cavity} = \text{field without dielectric} = E_{\text{other}} \]

Now
\[ E_{\text{other}} = E + \frac{\sigma_{\text{bound}}}{\varepsilon_0} = E + \frac{P}{\varepsilon_0} \]

For a sphere, \( E_{\text{other}} = E + \frac{P}{3\varepsilon_0} \)

so
\[ p = \alpha E_{\text{other}} = \alpha \left( E + \frac{P}{3\varepsilon_0} \right) \]

\[ P = n\alpha \left( E + \frac{P}{3\varepsilon_0} \right) = n\alpha \left( \frac{P}{(K-1)\varepsilon_0} + \frac{P}{3\varepsilon_0} \right) \]

\[ 3(K-1) = \frac{n\alpha}{\varepsilon_0}(3 + K - 1) \]

L5.7 Polarizability

Therefore
\[ \alpha = \frac{3\varepsilon_0 (K-1)}{n (K+2)} \]

This is the “Clausius-Mossotti equation”.

Note that \( \alpha = \frac{\varepsilon_0}{n}(K-1) \) if \( K \approx 1 \).

Examples: 1. Nitrogen gas, \( n=2.52 \times 10^{25} \text{ m}^{-3} \), \( K=1.00058 \).

Then \( \alpha/4\pi\varepsilon_0 = 1.83 \times 10^{-30} \text{ m}^3 \) using both formulas (since dilute). Experimentally, \( \alpha/4\pi\varepsilon_0 = 1.74 \times 10^{-30} \text{ m}^3 \).
2. Diamond.
If $P = 8 \times 10^{-6}$ Cm$^{-2}$, how far is centre of cloud of electrons from the nucleus?
Atomic wt =12, atomic number =6, density =3.51 x 10$^3$ kg m$^{-3}$.

Now $n=3.51 \times 10^3/(12 \times 1.66 \times 10^{-27}) =1.76 \times 10^{29}$ m$^{-3}$, and $P=np$, so
$p=8 \times 10^{-6}/(1.76 \times 10^{-29}) =4.55 \times 10^{-35}$ Cm =qd,
where $q =6 \times 1.6 \times 10^{-19}$ C,
so $d=4.55 \times 10^{-35}/(6 \times 1.6 \times 10^{-19}) =4.7 \times 10^{-17}$ m.
If $K =5.5$, $\alpha/4\pi\varepsilon_0 = 0.81 \times 10^{-30}$ m$^3$ (Clausius-Mossotti), and $\alpha/4\pi\varepsilon_0 = 2.03 \times 10^{-30}$ m$^3$ (dilute formula) different!