Lecture 16

Third-order nonlinear susceptibility $X^{(3)}$ and its tensor.

Third-order nonlinearity due to: fast electronic response, molecular re-orientation, electrostriction, thermal effects.

$\chi^{(3)}$ nonlinear susceptibility

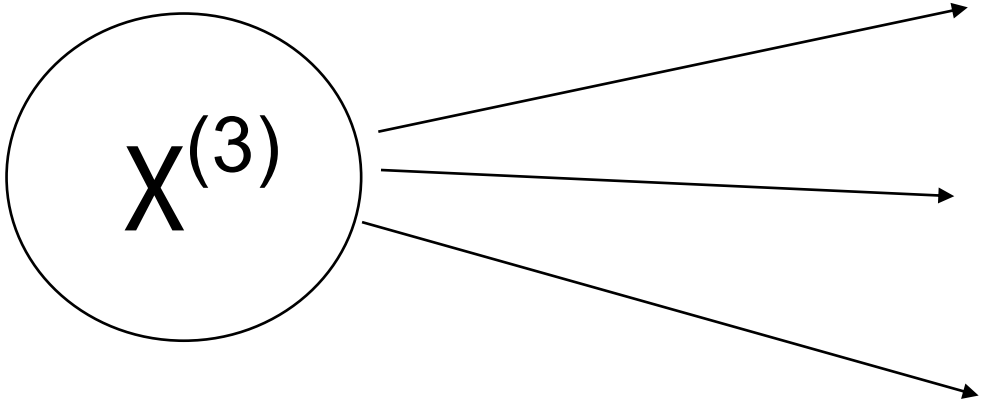
Formal definition of the nonlinear polarization:

$$\tilde{P}(t) = \epsilon_0\left[\chi^{(1)}\tilde{E}(t) + \chi^{(2)}\tilde{E}^2(t) + \chi^{(3)}\tilde{E}^3(t) + \cdots\right] \qquad \text{see (5.1)}$$

$$\equiv \tilde{P}^{(1)}(t) + \tilde{P}^{(2)}(t) + \tilde{P}^{(3)}(t) + \cdots .$$

ignoring dispersion of $\chi^{(3)}$

$$\boxed{P^{(3)}(t) = \chi^{(3)}E^3(t)} \qquad (16.1)$$



Two-photon Absorption
Nonlinear Refraction
Cross-phase modulation

3rd harmonic generation
Four-wave mixing

Stimulated Raman scattering
Stimulated Brillouin scattering
Phase conjugation

Linear $\chi^{(1)}$ Tensor

Recall linear media:

Linear susceptibility is a **tensor**

$$\mathbf{P} = \varepsilon_0 \boldsymbol{\chi} \mathbf{E}.$$

vector tensor vector

3x3=9 elements

$$P_i = \varepsilon_0 \sum_{j \in \{x,y,z\}} \chi_{ij} E_j$$

or

$$\begin{pmatrix} P_x \\ P_y \\ P_z \end{pmatrix} = \varepsilon_0 \begin{pmatrix} \chi_{xx} & \chi_{xy} & \chi_{xz} \\ \chi_{yx} & \chi_{yy} & \chi_{yz} \\ \chi_{zx} & \chi_{zy} & \chi_{zz} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix}$$

In an anisotropic medium, such as a crystal, the polarisation field *P* is not necessarily aligned with the electric field of the light *E*. In a physical picture, this can be thought of as the dipoles induced in the medium by the electric field having certain preferred directions, related to the physical structure of the crystal.

In nonmagnetic and transparent materials, $\boxed{\chi_{ij} = \chi_{ji}}$, i.e. the χ tensor is real and symmetric.

It is possible to diagonalise the tensor by choosing the appropriate coordinate axes, leaving only χ_{xx}, χ_{yy} and χ_{zz}.
This gives :

$$\begin{aligned} P_x &= \varepsilon_0 \chi_{xx} E_x \\ P_y &= \varepsilon_0 \chi_{yy} E_y \\ P_z &= \varepsilon_0 \chi_{zz} E_z \end{aligned}$$

Nonlinear $\chi^{(2)}$ Tensor

Recall quadratic media:

$$P_i^{(2)} = \epsilon_0 \sum_{j,k,l} \chi_{ijk} E_j E_k$$

3x3x3=27 elements

→ reduced to 18 elements

Nonlinear $\chi^{(3)}$ – Fourth rank tensor

Cubic nonlinearity media:

$$P_i^{(3)} = \epsilon_0 \sum_{j,k,l} \chi_{ijkl} E_j E_k E_l$$

3x3x3x3=81 elements

No symmetry restrictions: $\chi^{(3)} \neq 0$ in any material (even vacuum!)

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strictly speaking, $\chi_{ijkl} = \chi_{ijkl}(-\omega_4, \omega_1, \omega_2, \omega_3)$ (Stegeman)

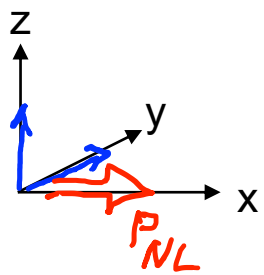
$$\omega_4 = \pm\omega_1 \pm \omega_2 \pm \omega_3$$

$$E_j = \frac{1}{2} E_j(\omega_j) e^{i\omega_j t} + c.c.$$
$$E_k = \frac{1}{2} E_k(\omega_k) e^{i\omega_k t} + c.c.$$
$$E_l = \frac{1}{2} E_l(\omega_l) e^{i\omega_l t} + c.c.$$

Symmetry properties of third-order susceptibilities

The symmetry properties of a material can reduce the number of $\chi^{(3)}$ elements drastically.

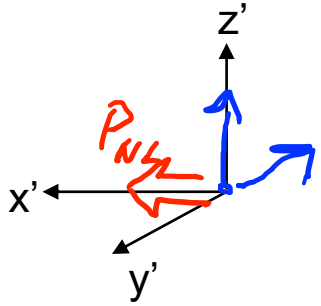
Why $\chi^{(3)}_{1223}$, is zero in isotropic media?



assume $E_y = 1,\ E_z = 1,$

then

$$P_x \sim \chi^{(3)}_{xyyz}\, E_y^2 E_z = \chi^{(3)}_{xyyz} \times 1 \times 1 \times 1 = 1 \times \chi^{(3)}_{xyyz}$$



In a coordinate system, which is rotated by 180 deg around z-axis: x'=-x; y'=-y; z'=z we get

$$P_{x'} \sim \chi^{(3)}_{x'y'y'z'}\, E^2_{y'} E_{z'} = \chi^{(3)}_{xyyz}\, E^2_{y'} E_{z'} == \chi^{(3)}_{xyyz} \times (-1) \times (-1) \times 1 = 1 \times \chi^{(3)}_{xyyz}$$

$$P_x \sim \chi^{(3)}_{1223}\, E_y^2 E_z \sim \chi^{(3)}_{xyyz}\, E_y^2 E_z$$

χ_{1223} → xyyz

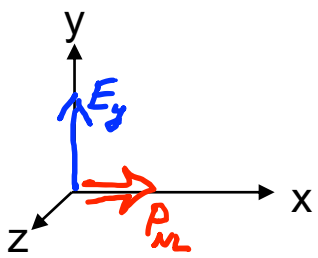
The result is that in the vector space $\boldsymbol{P}_{NL} = -\boldsymbol{P}_{NL}$

Hence $\chi^{(3)}_{xyyz} = \chi^{(3)}_{1223} = 0$

An index cannot appear an odd number of times in isotropic media

The symmetry properties of a material can reduce the number of $\chi^{(3)}$ elements drastically.

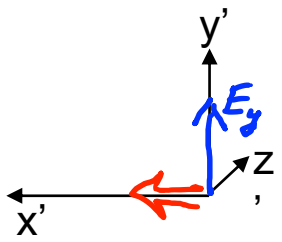
Why $\chi^{(3)}_{1222}$, is zero in isotropic media?



assume $E_y = 1$

then

$$P_x \sim \chi^{(3)}_{xyyy} E_y^3 = \chi^{(3)}_{xyyy} x1x1x1 = 1\chi^{(3)}_{xyyy}$$



In a coordinate system, which is rotated by 180 deg around y-axis: x'=-x; y'=y; z'=-z we get

$$P_{x'} \sim \chi^{(3)}_{x'y'y'y'} E_{y'}^3 = \chi^{(3)}_{xyyy} E_{y'}^3 == \chi^{(3)}_{xyyy} x1x1x1 = 1\chi^{(3)}_{xyyy}$$

$$P_x \sim \chi^{(3)}_{1222} P_y^3 \sim \chi^{(3)}_{xyyy} P_y^3$$

χ_{1222} → xyyy

The result is that in the vector space $\boldsymbol{P}_{NL} = -\boldsymbol{P}_{NL}$

for isotropic material, tensor elements should not depend on a system of coordinates

Hence $\chi^{(3)}_{xyyy} = \chi^{(3)}_{1222} = 0$

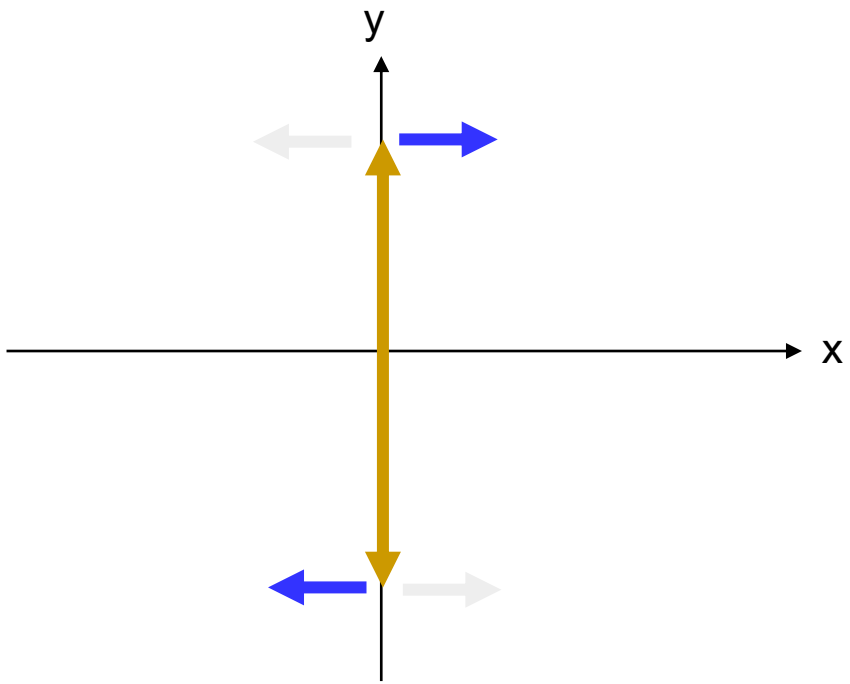
An index cannot appear an odd number of times in isotropic media

Symmetry properties of a material can reduce the number of $\chi^{(3)}$ elements drastically.

Another argument: χ_{1222} would give the response in the x direction due to a field applied in the y direction. This response must vanish in an isotropic material, because there is no reason why the response should be in the +x direction rather than in the −x direction.

$$P_x \sim E_y^3$$

χ_{1222} → xyyy → 0



An index cannot appear an odd number of times in isotropic media

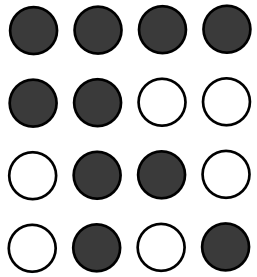
$\chi^{(3)}$ Tensor. Isotropic Media.

The symmetry properties of a material can reduce the number of elements.

In an isotropic medium, all coordinate systems are **equivalent**.

Therefore in terms of the subscripts ijkl , for the nonlinear coefficients we have:

simple case, all polarizations are parallel $P_x \sim E_x^3$ $etc.$



xxxx =yyyy=zzzz

yyzz=yyxx=xxzz=xxyy=zzxx=zzyy

xyyx=xzzx=yxxy=yzzy=zxxz=zyyz

xyxy=xzxz=yxyx=yzyz=zxzx=zyzy

No distinction between x, y, and z

same as:

$$\chi_{1111} = \chi_{2222} = \chi_{3333},$$

$$\chi_{1122} = \chi_{1133} = \chi_{2211} = \chi_{2233} = \chi_{3311} = \chi_{3322},$$

$$\chi_{1212} = \chi_{1313} = \chi_{2323} = \chi_{2121} = \chi_{3131} = \chi_{3232},$$

$$\chi_{1221} = \chi_{1331} = \chi_{2112} = \chi_{2332} = \chi_{3113} = \chi_{3223}.$$

No distinction between 1, 2, and 3

$\chi^{(3)}$ Tensor. **Any Media (even crystals)**

3x3x3x3=81 element

→

21 element

$\chi^{(3)}$ Tensor

We can **further reduce** the number of independent elements in isotropic media.

Any arbitrary rotation of a coordinate system must **lead to the same resulting nonlinear polarization** for the given input field directions.

Assume the general case of three parallel input fields E_1, E_2, and E_3 **copolarized along x-axis**, with different frequencies that produce the nonlinear polarization $P_x^{(3)}$ also **along x-axis**

$$P_x^{(3)} = \epsilon_0 \chi_{xxxx} E_1 E_2 E_3 \qquad (16.2)$$

χ_{xxxx} is the only tensor component that 'works' since all y and z components are zero

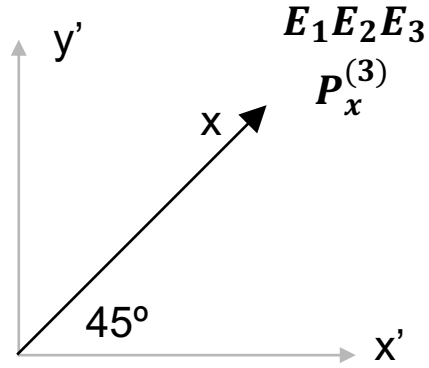
Now consider a new coordinate system (x', y') rotated 45° from the original in the xy plane.

The three input fields have the following components along the x'-axis and the y'-axis:

$$E_{1x'} = \frac{1}{\sqrt{2}} E_1; \;\; E_{1y'} = \frac{1}{\sqrt{2}} E_1;$$

$$E_{2x'} = \frac{1}{\sqrt{2}} E_2; \;\; E_{2y'} = \frac{1}{\sqrt{2}} E_2;$$

$$E_{3x'} = \frac{1}{\sqrt{2}} E_3; \;\; E_{3y'} = \frac{1}{\sqrt{2}} E_3;$$



$\chi^{(3)}$ Tensor

Now, it is clear that the nonlinear polarization vector $\boldsymbol{P}^{(3)}$ - should be the same in a new system.

Also, for isotropic material, tensor elements should not depend on a system of coordinates:

$$\chi^{(3)}_{xxxx} = \chi^{(3)}_{x'x'x'x'}$$
$$\chi^{(3)}_{xxyy} = \chi^{(3)}_{x'x'y'y'}$$
$$\chi^{(3)}_{xyyx} = \chi^{(3)}_{x'y'y'x'}$$
$$\chi^{(3)}_{xyxy} = \chi^{(3)}_{x'y'x'y'}$$

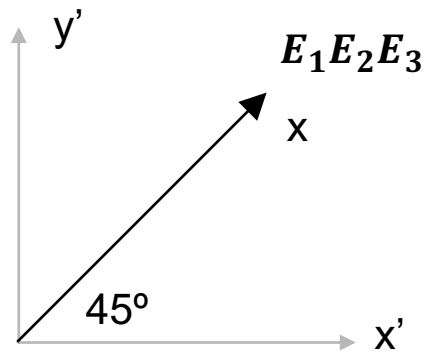
In a new system of coordinates (now we need to use 4 tensor components):

$$P^{(3)}_{x'} = \epsilon_0[\chi^{(3)}_{x'x'x'x'}E_{1x'}E_{2x'}E_{3x'} + \chi^{(3)}_{x'x'y'y'}E_{1x'}E_{2y'}E_{3y'}$$

$$+\chi^{(3)}_{x'y'y'x'}E_{1y'}E_{2y'}E_{3x'} + \chi^{(3)}_{x'y'x'y'}E_{1y'}E_{2x'}E_{3y'}] =$$

$$= \epsilon_0[\chi^{(3)}_{xxxx}E_{1x'}E_{2x'}E_{3x'} + \chi^{(3)}_{xxyy}E_{1x'}E_{2y'}E_{3y'}$$

$$+\chi^{(3)}_{xyyx}E_{1y'}E_{2y'}E_{3x'} + \chi^{(3)}_{xyxy}E_{1y'}E_{2x'}E_{3y'}] =$$



$\chi^{(3)}$ Tensor

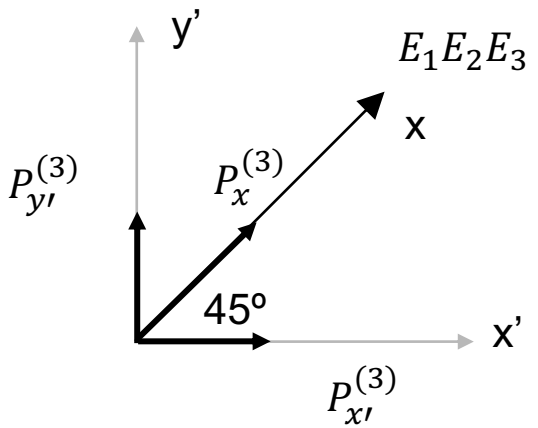
$$= \epsilon_0[\chi^{(3)}_{xxxx}E_{1x'}E_{2x'}E_{3x'}+\chi^{(3)}_{xxyy}E_{1x'}E_{2y'}E_{3y'}$$

$$+\chi^{(3)}_{xyyx}E_{1y'}E_{2y'}E_{3x'}+\chi^{(3)}_{xyxy}E_{1y'}E_{2x'}E_{3y'}]=$$

$$= \epsilon_0 \frac{1}{2\sqrt{2}}[\chi^{(3)}_{xxxx} + \chi^{(3)}_{xxyy} + \chi^{(3)}_{xyyx}+\chi^{(3)}_{xyxy}]E_1E_2E_3$$

In exactly the same way:

$$P^{(3)}_{y'} = \epsilon_0 \frac{1}{2\sqrt{2}}[\chi^{(3)}_{xxxx} + \chi^{(3)}_{xxyy} + \chi^{(3)}_{xyyx}+\chi^{(3)}_{xyxy}]E_1E_2E_3$$



By projecting $P^{(3)}_{y'}$ and $P^{(3)}_{y'}$ to the 'old' x-axis, we get :

$$P^{(3)}_{x} = \frac{1}{\sqrt{2}}(P^{(3)}_{x'}+P^{(3)}_{y'})= \epsilon_0 2\frac{1}{2\sqrt{2}}\frac{1}{\sqrt{2}}[\chi^{(3)}_{xxxx} + \chi^{(3)}_{xxyy} + \chi^{(3)}_{xyyx}+\chi^{(3)}_{xyxy}]E_1E_2E_3$$

$$= \epsilon_0 \frac{1}{2}[\chi^{(3)}_{xxxx} + \chi^{(3)}_{xxyy} + \chi^{(3)}_{xyyx}+\chi^{(3)}_{xyxy}]E_1E_2E_3 \qquad (16.3)$$

$\chi^{(3)}$ Tensor

By comparing $P_x^{(3)}$ obtained by two different ways, (16.2) and (16.3), that is in two coordinate systems, we get this relation between the third-order susceptibilities :

$$\frac{1}{2}[\chi_{xxxx}^{(3)} + \chi_{xxyy}^{(3)} + \chi_{xyyx}^{(3)} + \chi_{xyxy}^{(3)}] = \chi_{xxxx}^{(3)}$$

→

$$\boxed{\chi_{xxxx}^{(3)} = \chi_{xxyy}^{(3)} + \chi_{xyyx}^{(3)} + \chi_{xyxy}^{(3)}} \qquad (16.4)$$

same as

$$\boxed{\chi_{1111}^{(3)} = \chi_{1122}^{(3)} + \chi_{1221}^{(3)} + \chi_{1212}^{(3)}}$$

And all permutations of x-y-z, e.g. 1111→ 2222→ 3333 etc.

$$\chi_{1111} = \chi_{2222} = \chi_{3333},$$

$$\chi_{1122} = \chi_{1133} = \chi_{2211} = \chi_{2233} = \chi_{3311} = \chi_{3322},$$

$$\chi_{1212} = \chi_{1313} = \chi_{2323} = \chi_{2121} = \chi_{3131} = \chi_{3232}, \qquad (16.5)$$

$$\chi_{1221} = \chi_{1331} = \chi_{2112} = \chi_{2332} = \chi_{3113} = \chi_{3223}.$$

$\chi^{(3)}$ Tensor

These are universal relation for isotropic media – true for any set of input frequencies, on or off resonance.

The number of independent elements is reduced to 3 – true for all isotropic media, including liquids, gases of molecules or electrons.

In the case of Kleinman symmetry (optical frequencies are well below resonances) permutation symmetry applies: *ijkl* → *jikl* → *ijlk* → *ikjl* ... etc...

And we get:

$$\chi^{(3)}_{xxyy} = \chi^{(3)}_{xyyx} = \chi^{(3)}_{xyxy} = \frac{1}{3}\chi^{(3)}_{xxxx} \qquad (16.5)$$

only 1 tensor element is independent

$\chi^{(3)}$ Tensor: **crystals**

For GaAs crystal ($\bar{4}$3m symmetry, cubic crystal) **only 4 tensor elements** are independent

$$xxxx = yyyy = zzzz$$

$$yyzz = zzxx = xxyy = zzyy = xxzz = yyxx$$

$$yzzy = zxxz = xyyx = zyyz = xzzx = yxxy$$

$$yzyz = zxzx = xyxy = zyzy = xzxz = yxyx$$

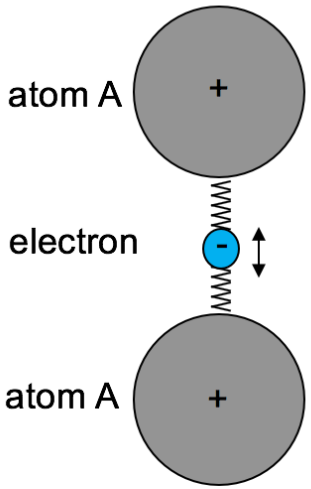
Examples of third-order processes

Intensity- dependent refraction index is the most typical manifestation of $\chi^{(3)}$ effects

$X^{(3)}$ due to fast electronic response

Recall Lecture 3

Nonlinear Susceptibility of a Classical Anharmonic Oscillator

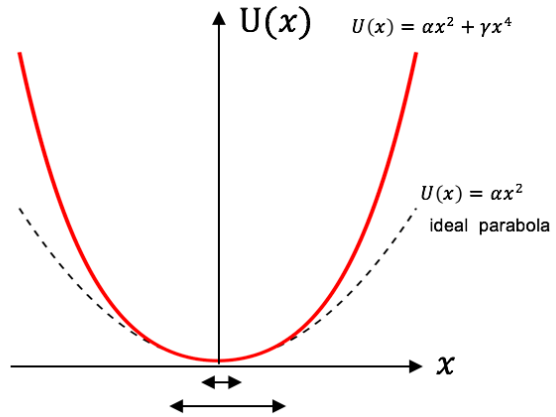


Centrosymmetric Media
– e.g. liquids, gases, amorphous solids (such as glass), and many crystals (such as Si, Ge etc.)

There is no cubic term in *U*(x) :

$$U(x) = \alpha x^2 + \gamma x^4 + \ldots$$

As a cosequence, such effects as second-harmonic generation and optical rectification (and also piezoelectric effect) are forbidden.



Third-harmonic generation

Using similar formalism, one can show that high excitation field produces the nonlinear polarization oscillating at frequency 3ω (in addition to the one oscillating at ω).

$X^{(3)}$ due to fast nonresonant electronic response (e.g. alkali metal vapors)

Nonresonant electronic nonlinearities occur as the result of the nonlinear response of bound electrons to an applied optical field. This nonlinearity usually is not particularly large but is of considerable importance because it is present in all dielectric materials.

The third-order susceptibility describing the nonlinear refractive index can be described using the laws of **quantum mechanics** and a 4-level model system.

$$\omega_\sigma = \omega_p + \omega_q + \omega_r$$

$$\chi^{(3)}_{kjih}(\omega_\sigma, \omega_r, \omega_q, \omega_p) = \frac{N}{\epsilon_0 \hbar^3} \mathcal{P}_F \sum_{mnv} \frac{\mu^k_{gv}\mu^j_{vn}\mu^i_{nm}\mu^h_{mg}}{(\omega_{vg} - \omega_\sigma)(\omega_{ng} - \omega_q - \omega_p)(\omega_{mg} - \omega_p)}$$

transition dipole momenta

The 24 permutations denoted by the operator P_F are:

$(\omega_\sigma, \omega_p, \omega_q, \omega_r)$	$(\omega_p, \omega_\sigma, \omega_q, \omega_r)$
$(\omega_\sigma, \omega_p, \omega_r, \omega_q)$	$(\omega_p, \omega_\sigma, \omega_r, \omega_q)$
$(\omega_\sigma, \omega_q, \omega_p, \omega_r)$	$(\omega_p, \omega_q, \omega_\sigma, \omega_r)$
$(\omega_\sigma, \omega_q, \omega_r, \omega_p)$	$(\omega_p, \omega_q, \omega_r, \omega_\sigma)$
$(\omega_\sigma, \omega_r, \omega_p, \omega_q)$	$(\omega_p, \omega_r, \omega_\sigma, \omega_q)$
$(\omega_\sigma, \omega_r, \omega_q, \omega_p)$	$(\omega_p, \omega_r, \omega_q, \omega_\sigma)$
.....	.....
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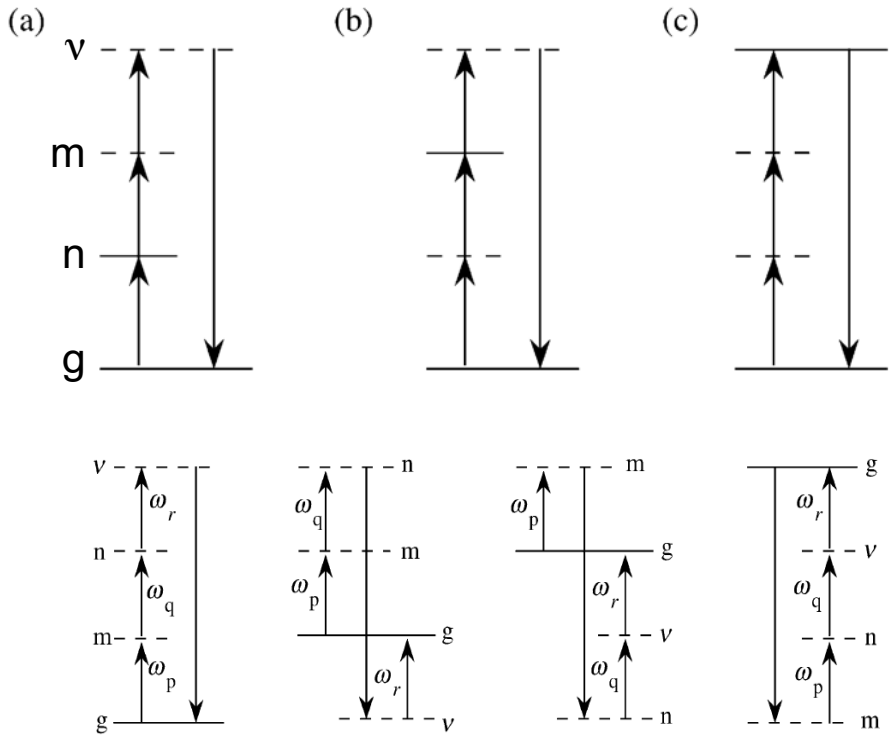
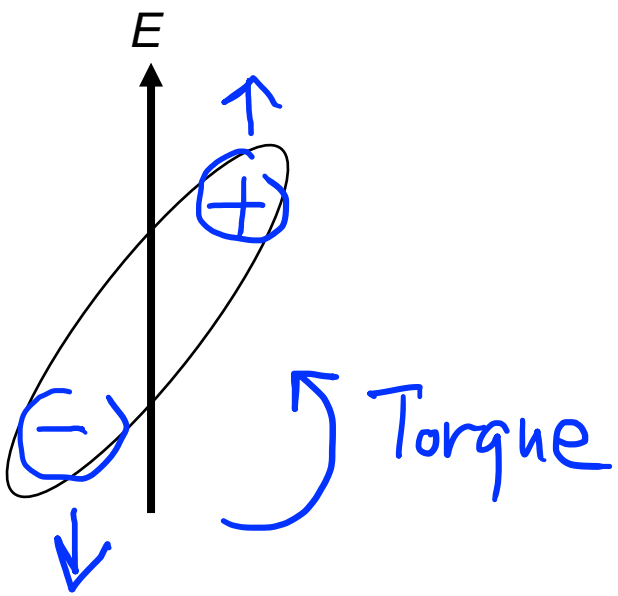
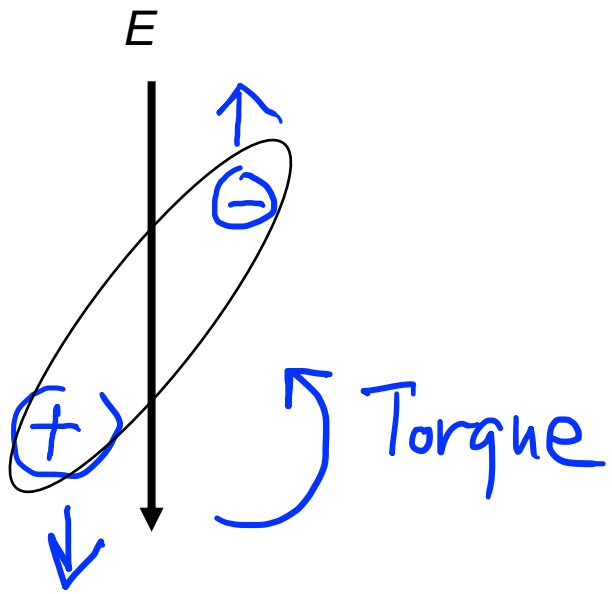


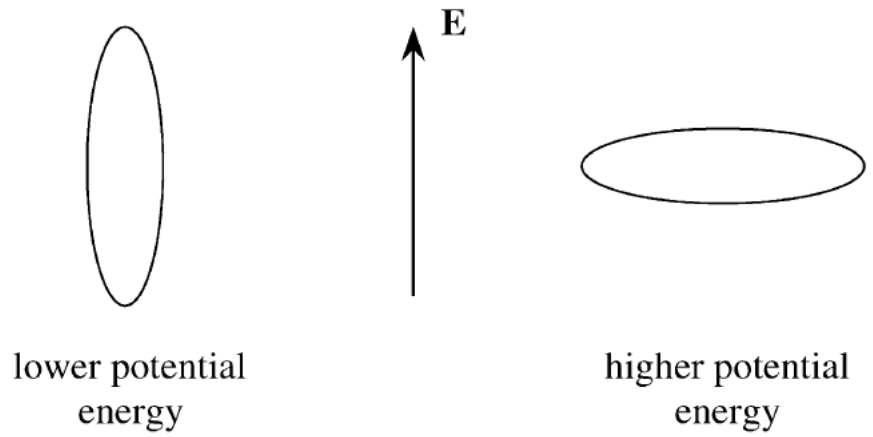
$X^{(3)}$ due to **molecular re-orientation**

Liquids that are composed of anisotropic molecules (i.e., molecules having an anisotropic polarizability tensor) typically possess a large value of n_2. Example: CS_2 molecule. The origin of this nonlinearity is the tendency of molecules to become aligned in the electric field of an applied optical wave. The optical wave then experiences a modified value of the refractive index because the average polarizability per molecule has been changed by the molecular alignment.

CS_2



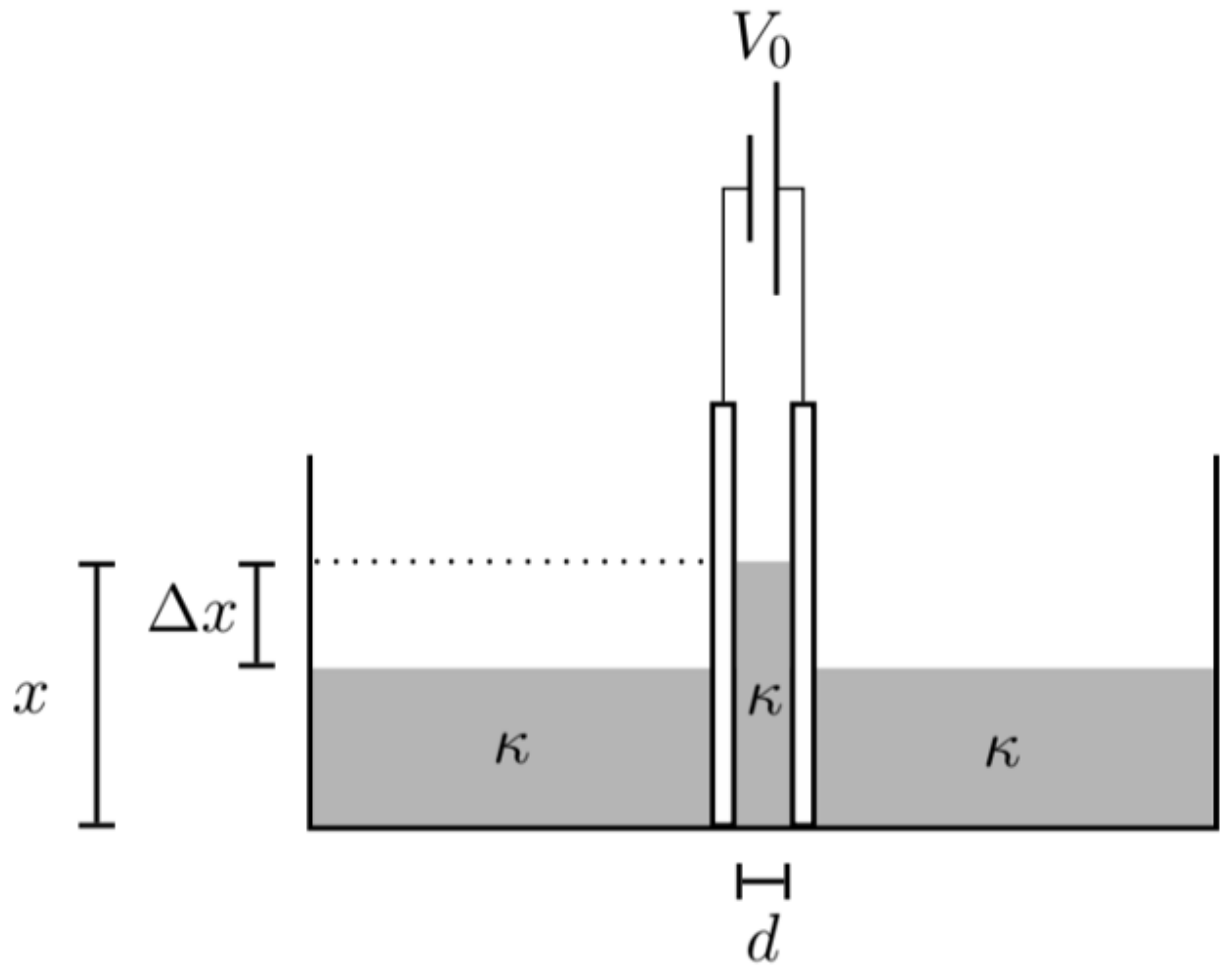




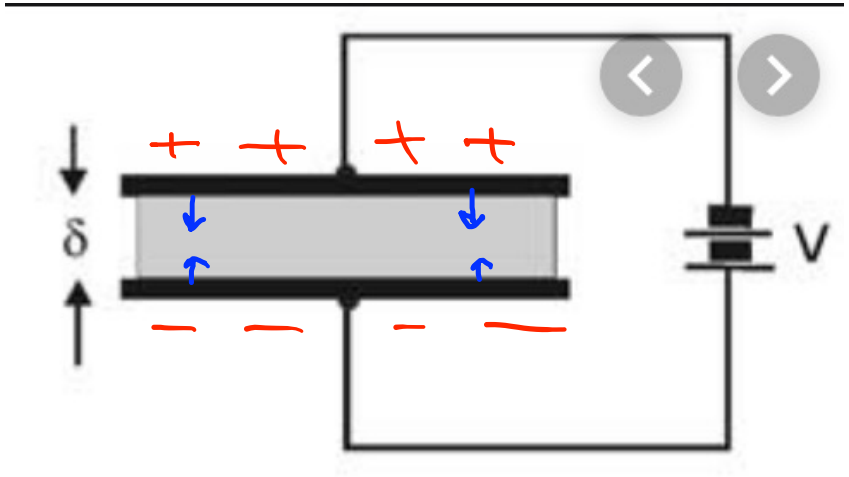
This torque is directed in such a manner as to twist the molecule into alignment with the applied electric field.

$X^{(3)}$ due to **electrostriction**

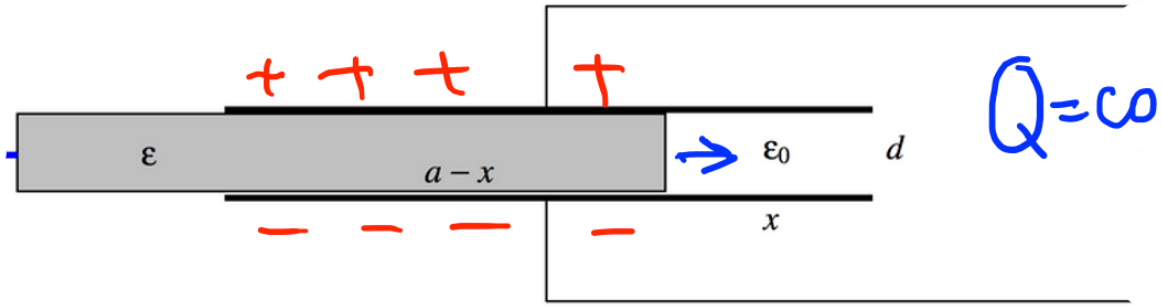
Liquid is sucked in between the plates of a charged capacitor



$X^{(3)}$ due to **electrostriction**



Consider an electrical capacitor with two parallel plates. When an electric field is applied, charges are induced on the plates with opposite signs on opposite plates. Due to the presence of the positive and negative charges, there is a **compressive force squeezing the medium** that produces a strain field. This results in a material contraction and hence change in the refractive index.



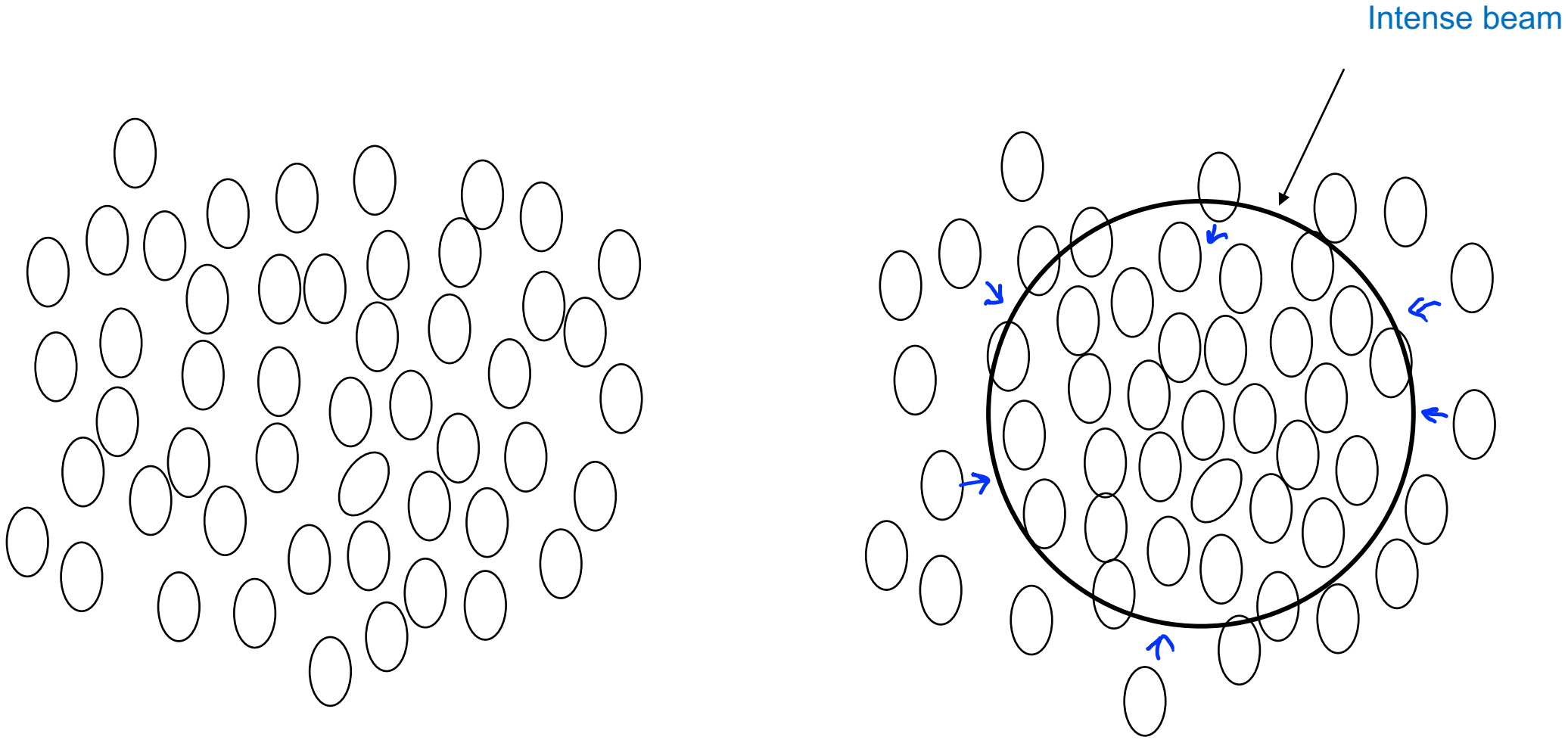
Q=const

energy $\mathcal{E} = \frac{Q^2}{2C}$ $C = \frac{\varepsilon\varepsilon_0 A}{d}$

ε-increases → $\mathcal{E}$ decreases

Another effect is that a **dielectric will be sucked into a capacitor** because it reduces the total energy

$X^{(3)}$ due to electrostriction



The effect is ~ E^2

$X^{(3)}$ due to **thermal effects**

Thermal processes can lead to large nonlinear optical effects. The origin of thermal nonlinear optical effects is that some fraction of the incident laser power is absorbed in passing through an optical material. The temperature of the illuminated portion of the material consequently increases, which leads to a change in the refractive index of the material. For gases, the refractive index invariably decreases with increasing temperature (at constant pressure), but for condensed matter the refractive index can either increase or decrease with changes in temperature.

The time scale for changes in the temperature of the material can be quite long (of the order of seconds), and consequently thermal effects often lead to strongly time-dependent nonlinear optical phenomena.