Lecture 16

Third-order nonlinear susceptibility $\chi^{(3)}$ and its tensor. Third-order nonlinear due to: fast electronic response, molecular re-orientation, electrostriction, thermal effects. $\chi^{(3)}$ in semiconductors.

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

Formal definition of the nonlinear polarization:

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

$$\equiv \tilde{P}^{(1)}(t) + \tilde{P}^{(2)}(t) + \tilde{P}^{(3)}(t) + \cdots.$$  \hspace{1cm} (5.1)

Ignoring dispersion of $\chi^{(3)}$.

$$P^{(3)}(t) = \chi^{(3)} E^3(t)$$  \hspace{1cm} (16.1)
\( \chi^{(1)} \) Tensor

Recall linear media:

Linear susceptibility is a tensor

\[
P = \varepsilon_0 \chi E,
\]

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, \( \chi_{ij} = \chi_{ji} \) i.e. the \( \chi \) tensor is real and symmetric.

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

\[
\begin{align*}
P_x &= \varepsilon_0 \chi_{xx} E_x \\
P_y &= \varepsilon_0 \chi_{yy} E_y \\
P_z &= \varepsilon_0 \chi_{zz} E_z \\
\end{align*}
\]

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

Recall quadratic media:

\[
P^{(2)}_i = \varepsilon_0 \sum_{j,k,l} \chi_{ijk} E_j E_k
\]

3x3x3=27 elements

\[ \Rightarrow 18 \text{ elements} \]
$$\chi^{(3)} - \text{Fourth rank tensor}$$

Cubic nonlinearity media:

$$P_i^{(3)} = \varepsilon_0 \sum_{j,k,l} \chi_{ijkl} E_j E_k E_l \quad 3x3x3x3=81 \text{ elements}$$

No symmetry restrictions: $\chi_{ijkl} \neq 0$ in any material

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
\( \chi^{(3)} \) Tensor: why \( \chi^{(3)}_{1222} , \chi^{(3)}_{1223} \) etc. are zeros?

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

An index cannot appear an odd number of times, because, for example, \( \chi_{1222} \) 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.

\[ \chi_{1222} \rightarrow xyyyy \]

\[ P_x \sim P_y^3 \]

Isotropic Media.

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

In an isotropic medium, all coordinate systems are equivalent.

Therefore in terms of the subscripts \( ijk \), for the nonlinear coefficients we have:

- \( xxxx = yyyy = zzzz \)
- \( yyzz = yyxx = xxzz = xxyy = zzxx = zzyy \)
- \( xyyx = xzzx = yxyx = yzzy = zxxz = zyyz \)
- \( xxyx = xzxz = yxyz = yzyz = zxzx = zzyy \)

No distinction between x, y, and z

\[ \begin{align*}
\chi_{1111} &= \chi_{2222} = \chi_{3333}, \\
\chi_{1122} &= \chi_{1133} = \chi_{2211} = \chi_{2233} = \chi_{3311} = \chi_{3322}, \\
\chi_{1212} &= \chi_{1313} = \chi_{2323} = \chi_{2121} = \chi_{3113} = \chi_{3232}, \\
\chi_{1221} &= \chi_{1331} = \chi_{2112} = \chi_{2332} = \chi_{3113} = \chi_{3223}.
\end{align*} \]
\( \chi^{(3)} \) Tensor

3x3x3x3 = 81 element

\[ \rightarrow \]

21 element

\[ \begin{align*}
\chi_{\text{XXX}} &= \chi_{\text{YYY}} = \chi_{\text{ZZZ}} \\
\chi_{\text{YYZ}} &= \chi_{\text{YXX}} = \chi_{\text{XYY}} = \chi_{\text{ZYZ}} \\
\chi_{\text{XYX}} &= \chi_{\text{XZXY}} = \chi_{\text{YXZ}} = \chi_{\text{ZYX}} \\
\chi_{\text{XZX}} &= \chi_{\text{ZXZ}} = \chi_{\text{YZZ}} = \chi_{\text{ZZY}} \end{align*} \]

\( \chi^{(3)} \) 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. This leads to a simple relation between the tensor coefficients.

Assume the general case of three, parallel, copolarized along x-axis, input fields \( \mathbf{E}_1 \), \( \mathbf{E}_2 \), and \( \mathbf{E}_3 \) with different frequencies that produce the nonlinear polarization \( P_x^{(3)} \) along x-axis

\[ P_x^{(3)} = \epsilon_0 \chi_{\text{XXX}} E_1 E_2 E_3 \]  \hspace{1cm} (16.2)

\( \chi_{\text{XXX}} \) 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:

\[ E_{1x'} = \frac{1}{\sqrt{2}} E_1; \quad E_{1y'} = \frac{1}{\sqrt{2}} E_1; \]
\[ E_{2x'} = \frac{1}{\sqrt{2}} E_2; \quad E_{2y'} = \frac{1}{\sqrt{2}} E_2; \]
\[ E_{3x'} = \frac{1}{\sqrt{2}} E_3; \quad E_{3y'} = \frac{1}{\sqrt{2}} E_3; \]
χ(3) Tensor

Now, it is clear that the result for the nonlinear polarization $p^{(3)}$ should be the same in a new system.

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

$\chi_{xx}^{(3)} = \chi_{xx}^{(3)}$,
$\chi_{xy}^{(3)} = \chi_{xy}^{(3)}$,
$\chi_{yy}^{(3)} = \chi_{yy}^{(3)}$,
$\chi_{yx}^{(3)} = \chi_{yx}^{(3)}$.

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

$P_{x'}^{(3)} = \epsilon_0[\chi_{xxxx}E_{1x}E_{2x}E_{3x} + \chi_{xxyy}E_{1x}E_{2y}E_{3y} + \chi_{xyxy}E_{1y}E_{2x}E_{3y} + \chi_{yxxy}E_{1y}E_{2y}E_{3x}]$

$= \epsilon_0[\chi_{xxxx}E_{1x}E_{2x}E_{3x} + \chi_{xxyy}E_{1x}E_{2y}E_{3y} + \chi_{xyxy}E_{1y}E_{2x}E_{3y} + \chi_{yxxy}E_{1y}E_{2y}E_{3x}]$

$= \epsilon_0 \frac{1}{\sqrt{2}} [\chi_{xxxx} + \chi_{xxyy} + \chi_{xyxy} + \chi_{yxxy}] E_1 E_2 E_3$

In exactly the same way:

$P_{y'}^{(3)} = \epsilon_0 \frac{1}{\sqrt{2}} [\chi_{xxxx} + \chi_{xxyy} + \chi_{xyxy} + \chi_{yxxy}] E_1 E_2 E_3$

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

$P_{x}^{(3)} = \frac{1}{\sqrt{2}} (P_{x'}^{(3)} + P_{y'}^{(3)}) = \epsilon_0 \frac{1}{\sqrt{2}} \frac{1}{\sqrt{2}} [\chi_{xxxx} + \chi_{xxyy} + \chi_{xyxy} + \chi_{yxxy}] E_1 E_2 E_3$

$= \epsilon_0 \frac{1}{2} [\chi_{xxxx} + \chi_{xxyy} + \chi_{xyxy} + \chi_{yxxy}] E_1 E_2 E_3$

(16.3)
**χ(3) Tensor**

By comparing $p^{(3)}$ 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:

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

$$\Rightarrow$$

$$\chi_{xxxx}^{(3)} = \chi_{xyyx}^{(3)} + \chi_{xyxy}^{(3)}$$

same as

$$\chi_{1111}^{(3)} = \chi_{1222}^{(3)} + \chi_{1212}^{(3)}$$

(16.4)

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

$$\chi_{1111} = \chi_{2222} = \chi_{3333},$$
$$\chi_{1122} = \chi_{1133} = \chi_{2211} = \chi_{2233} = \chi_{3311} = \chi_{3322},$$
$$\chi_{1212} = \chi_{1313} = \chi_{2323} = \chi_{2121} = \chi_{3131} = \chi_{3232},$$
$$\chi_{1221} = \chi_{1331} = \chi_{2112} = \chi_{2332} = \chi_{3113} = \chi_{3223}.$$

(16.5)

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 $\rightarrow$ jikl $\rightarrow$ ijk $\rightarrow$ ikjl ... etc...

And we get:

$$\chi_{xyyx}^{(3)} = \chi_{xyxy}^{(3)} = \chi_{xyyx}^{(3)} = \frac{1}{3} \chi_{xxxx}^{(3)}$$

(16.5)
\( \chi^{(3)} \) Tensor: crystals

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

\[
\begin{align*}
xxxx &= yyyy = zzzz \\
yyzz &= zxxx = xyy = zzyy = xxzz = yyxx \\
yzzy &= zxzz = xyyx = zyyz = xzzx = yxx \\
yzyz &= zzxx = xyxy = zyxz = xzxx = yxyx
\end{align*}
\]

Examples of third-order processes

Intensity-dependent refraction 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 $U(x)$:
$$U(x) = \alpha x^2 + \gamma x^4 + ..$$

As a consequence, 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 $3\omega$ (in addition to the one oscillating at $\omega$).

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

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.
**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.

![Diagram of molecular re-orientation](image)

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

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**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.

![Diagram of electrostriction](image)

Another effect is that a dielectric will be sucked into a capacitor because it reduces the total energy.
For $\hbar \omega > E_g$, the nonlinear response occurs as the result of band-to-band transitions. Electrons in the conduction band can be considered to respond freely to an applied optical field. The free electron contribution to the dielectric constant is:

$$\varepsilon(\omega) = \varepsilon_b - \frac{\omega_p^2}{\omega(\omega + i/\tau)}.$$

For $\hbar \omega < E_g$, the nonlinear response involves virtual processes.
**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.