Module 2 : Nonlinear Frequency Mixing

Lecture 8 : Nonlinear Susceptibility Tensors

Objectives

In this lecture we will look at

- Susceptibility tensors and response functions.
- Their general properties.
- Spatial symmetry properties.

In the discussion of the linear response of an electron in harmonic oscillator potential, we had seen that the Fourier component $P(\omega)$ of the polarization is directly proportional to $E(\omega)$ but the constant of proportionality, the linear susceptibility, depends on the frequency ω. Using the convolution theorem this yields a relation between polarization and field as:

$$P(t) = \int_0^\infty d\tau R(\tau) E(t-\tau) \tag{8.1}$$

with

$$\varepsilon_0 \chi(\omega) = \int_0^\infty d\tau e^{-i\omega_1 \tau} R(\tau) \tag{8.2}$$

Allowing for anisotropy in 3 dimensional media, this generalizes to

$$P_\mu(t) = \int_0^\infty d\tau R_{\mu\alpha}(\tau) E_\alpha(t-\tau) \tag{8.3}$$

where μ and α denote cartesean components and summation over repeated indices is understood.

As discussed in Lectures 1 and 7, the polarization is, in general, nonlinear function of field. For moderate fields, the perturbation series for polarization $\vec{P}$ may be written as

$$\vec{P} = \vec{P}^{(1)} + \vec{P}^{(2)} + \vec{P}^{(3)} \ldots$$

where the superscript denotes the order in $|\vec{E}|$, i.e. successive terms in the above series are smaller by a factor ~E/E_{atom} where E_{atom} is the electric field seen by the polarizable electrons in an unperturbed atom. Most generally, one can write the nth order polarization as

$$P_\mu^{(n)}(t) = \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \ldots \int_0^\infty d\tau_n R^{(n)}_{\mu\alpha_1 \ldots \alpha_n}(\tau_1, \tau_2, \ldots \tau_n) E_{\alpha_1}(t-\tau_1) E_{\alpha_2}(t-\tau_2) \ldots E_{\alpha_n}(t-\tau_n) \tag{8.4}$$

where summation over repeated indices is understood and $\mu, \alpha_1, \ldots \alpha_n$ denote Cartesian coordinates. Polarization $\vec{P}(t)$ depends only on the fields at all previous times. (Causality i.e. a response always follows a stimulus- means here that the polarization at time t cannot depend on fields at times t'>t). For the response function $R^{(n)}$ to be unambiguously defined, it must be symmetric under exchange of dummy variables/ indices i.e $R^{(n)}_{\mu\alpha_1 \ldots \alpha_n}(\tau_1, \ldots \tau_n)$ must be invariant under exchange of $\alpha_1\tau_1, \alpha_2\tau_2 \ldots \alpha_n\tau_n$ since $R^{(n)}_{\mu\alpha_1 \ldots \alpha_n}(\tau_1, \ldots \tau_n)$ is the coefficient of the product $E_{\alpha_1}(t-\tau_1) E_{\alpha_2}(t-\tau_2) \ldots E_{\alpha_n}(t-\tau_n)$ which does not change if any pairs of indices are exchanged. The nth order susceptibility tensor $\chi^{(n)}$ is Fourier transform of $R^{(n)}$.

$$\varepsilon_0 \chi^{(n)}_{\mu\alpha_1 \ldots \alpha_n}(\omega_1, \omega_2, \ldots \omega_n) = \int_0^\infty d\tau_1 \ldots d\tau_n e^{-i(\omega_1\tau_1 \ldots + \omega_n\tau_n)} R^{(n)}_{\mu\alpha_1 \ldots \alpha_n}(\tau_1, \ldots, \tau_n) \tag{8.5}$$

To see this, we start from

$$P_\mu^{(n)}(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} P_\mu^{(n)}(t)\, e^{+i\omega t} dt$$

$$= \frac{1}{2\pi}\int_{-\infty}^{\infty} dt \int_0^{\infty} d\tau_1 \ldots d\tau_n R^{(n)}_{\mu\alpha_1\ldots\alpha_n}(\tau_1 \ldots \tau_n) E_{\alpha_1}(\omega_1) e^{+i\omega_1(\tau_1 - t)} \ldots E_{\alpha_n}(\omega_n) e^{i\omega_n(\tau_n - t)} e^{i\omega t} \qquad (8.6)$$

We put $R^{(n)}_{\mu\alpha_1\ldots\alpha_n}(\tau_1 \ldots \tau_n) = 0$ for $\tau_1 \text{or} \tau_2 \ldots\ldots \text{or}\ \tau_n < 0$ the range of integration can then be taken as $-\infty$ to ∞. So

$$P_\mu^{(n)}(\omega) = \sum_{\omega_1 \ldots \omega_n} \frac{1}{2\pi}\int_{\infty}^{\infty} dt\, e^{-i(\omega_1+\omega_2\ldots\omega_n-\omega)t}$$

$$\int_{-\infty}^{\infty} d\tau_1 \ldots d\tau_n\, R^{(n)}_{\mu\alpha_1\ldots\alpha_n}(\tau_1 \ldots \tau_n) e^{i(\omega_1\tau_1+\omega_2\tau_2\ldots\omega_n\tau_n)} E_{\alpha_1}(\omega_1) E_{\alpha_2}(\omega_2) \ldots E_{\alpha_n}(\omega_n) \qquad (8.7)$$

$$= \varepsilon_0 \delta(\omega - (\omega_1 + \ldots \omega_n)) \chi^{(n)}_{\mu\alpha_1\ldots\alpha_n}(\omega_1 \ldots \omega_n) E_{\alpha_1}(\omega_1) \ldots\ldots E_{\alpha_n}(\omega_n)$$

The combined action of fields at frequencies $\omega_1, \ldots \omega_n$ generates a frequency $\omega_1 + \omega_2 + \ldots \omega_n = \omega$ (say). To make this explicit. $\chi^{(n)}_{\mu\alpha_1\ldots\alpha_n}(\omega_1, \ldots \omega_n)$ is often written as $\chi^{(n)}_{\mu\alpha_1\ldots\alpha_n}(-\omega, \omega_1, \ldots \omega_n)$.

Quite often, we treat incident waves as monochromatic i.e. ignore their spectral width. We then write

$$\vec{\mathrm{E}}(t) = \sum_i \left(\vec{E}(\omega_i)\, e^{-i\omega t} + c.c.\right) \qquad (8.8)$$

$$\vec{\mathrm{E}}(\omega) = \sum_i \left(\vec{E}(\omega_i)\, \delta(\omega - \omega_i) + \vec{E}^*(\omega_i)\, \delta(\omega + \omega_i)\right) \qquad (8.9)$$

Thus, the Eq. (8.7) becomes

$$P_\mu^{(n)}(\omega) = \varepsilon_0 N_d\, \chi^{(n)}_{\mu\alpha_1\ldots\alpha_n}(\omega_1, \ldots \omega_n) E_{\alpha_1}(\omega_1) \ldots E_{\alpha_n}(\omega_n) \delta_{\omega_1, \omega_1+\omega_2+\ldots\omega_n} \qquad (8.10)$$

where N_d is the number of distinct permutation of frequency $\omega_1 \ldots\ldots\ldots \omega_n$. For example, for SHG the susceptibility involved is $\overleftrightarrow{\chi}^{(2)}(\omega, \omega)$

$$P_\mu^{(n)}(2\omega) = N_d\, \chi^{(2)}_{\mu\alpha_1\ldots\alpha_1}(-2\omega, \omega, \omega) E_{\alpha_1}(\omega_1) E_{\alpha_1}(\omega)$$

In this can N_d is 1 since there is only one distinct combination of frequencies. For sum frequency generation, on the other hand

$$P_\mu^{(2)}(\omega_1 + \omega_2) = 2\, \chi^{(2)}_{\mu\alpha_1\ldots\alpha_2}(-\omega_1 - \omega_2, \omega_1, \omega_2) E_{\alpha_1}(\omega_1) E_{\alpha_2}(\omega_2)$$

Symmetry of $R^{(n)}_{\mu\alpha_1\ldots\alpha_n}(Z_1 \ldots Z_n)$ under exchange of pairs $\alpha_1 Z_1, \ldots \alpha_n Z_n$ implies $\chi^{(n)}_{\mu\alpha_1\alpha_2\ldots\alpha_n}(-\omega, \omega_1, \omega_2 \ldots \omega_n) = \chi^{(n)}_{\mu\alpha_2\alpha_1\ldots\alpha_n}(-\omega, \omega_2, \omega_1 \ldots \omega_n)$ i.e. $\chi^{(n)}_{\mu\alpha_1\alpha_2\ldots\alpha_n}(-\omega, \omega_1, \omega_2 \ldots \omega_n)$ is invariant under exchange of $\alpha_1\omega_1, \alpha_2\omega_2, \ldots \alpha_n\omega_n$.

Since $\vec{P}(t), \vec{E}(t)$ are real $\therefore R^{(n)}$ are also real which in turn implies that

$$\chi^{(n)}_{\mu\alpha_1\ldots\alpha_n}(-\omega, \omega_1, \ldots \omega_n) = \chi^{(n)*}_{\mu\alpha_1\ldots\alpha_n}(\omega, -\omega_1, \ldots -\omega_n) \qquad (8.11)$$

Note: In the perturbation theory calculation of susceptibilities in the steady state we often switch on the perturbation adiabatically i.e. with a factor $e^{\varepsilon t}$ with $\varepsilon \to +0$ (In the anharmonic oscillator model the damping factor plays the same role.) If this factor is included then all ω become complex and $-\omega_i$ have to be replaced by $-\omega_i^*$ on the right hand side in above equation.

In fact, away from all resonances $\chi^{(n)}_{\mu\alpha_1\ldots\alpha_n}(-\omega, \omega_1, \omega_2, \ldots \omega_n)$ is also symmetric under the exchange of pair

$\mu-\omega$, with $\alpha_1\omega_1,\alpha_2\omega_2\ldots\alpha_n\omega_n$. This relation can be seen from the perturbation series expressions for $\chi^{(n)}$. It can also be obtained by writing the interaction energy for the interaction between $(n+1)$ waves that $\chi^{(n)}$ represents.

[Ref: P.S. Pershan Phys. Rev **130**,919(1963)]

The overall permutation symmetry i.e. invariance of $\chi^{(n)}_{\mu\alpha_1\ldots\alpha_n}(-\omega,\omega_1,\omega_2,\ldots\omega_n)$ under exchange of $(n+1)$ pairs $\mu-\omega,\alpha_1\omega_1,\alpha_2\omega_2\ldots\alpha_n\omega_n$ has important physical implications. For example, $\chi^{(2)}_{\mu\alpha\beta}(-(\omega_1+\omega_2),\omega_1,\omega_2)$ describes, sum frequency generation at from waves at ω_1 and ω_2. This is equal to $\chi^{(2)}_{\alpha\mu\beta}(+\omega_1,-(\omega_1+\omega_2),\omega_2)=\chi^{(2)*}_{\alpha\mu\beta}(-\omega_1,\omega_1+\omega_2,-\omega_2)$ (by reality condition) which describes the different frequency generation of ω_1 from incident waves at $\omega_1+\omega_2$ and ω_2. Similarly, the nonlinear optical rectification is described by $\chi^{(2)}_{\mu\alpha\beta}(0,\omega,-\omega)$ is related to the electro optic effect described by $\chi^{(2)}_{\beta\alpha\mu}(-\omega,\omega,0)$.

The nonlinear susceptibility $\chi^{(n)}_{\mu\alpha_1\ldots\alpha_n}(-\omega,\omega_1\ldots\omega_n)$ is a function of only n input frequency $\omega_1\ldots\ldots\ldots\omega_n$ So, why is it written as a function of n+1 frequencies? The reason is that the process of generation of $\omega_3=\omega_1+\omega_2$ from two inputs at frequency ω_1 and ω_2 is described by the same susceptibility tensor that describes the generation of $\omega_1=\omega_3-\omega_2$ from input frequencies ω_3 and ω_2 due to the overall permutation symmetry. It is to reflect this important aspect the generated frequency is added as variable in the susceptibility tensor and the process is called ***three wave mixing***. As we shall see later, this symmetry is important in 3 wave mixing process and yields Manley Relations.

Spatial Symmetry

$\vec{\vec{\chi}}^{(n)}$ is a tensor of rank n+1 characterizing medium. If the medium (represented by its Hamiltonian) remains invariant under a coordinate transformation then $\vec{\vec{\chi}}^{(n)}$ should also remain unchanged as a result of this transformation. Thus if the material remains invariant under a rotation of axes given by

$$\begin{pmatrix}x_1\\x_2\\x_3\end{pmatrix}=\begin{pmatrix}a_{11}&a_{12}&a_{13}\\a_{21}&a_{22}&a_{23}\\a_{31}&a_{32}&a_{33}\end{pmatrix}\begin{pmatrix}x_1'\\x_2'\\x_3'\end{pmatrix} \tag{8.12}$$

Then

$$\chi^{(n)}_{\mu\alpha_1\ldots\alpha_n}=a_{\mu\mu'}a_{\alpha_1\alpha_1'}\ldots a_{\alpha_n\alpha_n'}\chi^{(n)}_{\mu'\alpha_1'\ldots\alpha_n'} \tag{8.13}$$

(Frequencies remain same on both sides)

Here a_{ij} is the cosine of the angle between OX_i and OX_j'. a_{ij} are called direction cosines. The direction cosines satisfy the relations

$$\sum_j a_{ij}a_{kj}=\delta_{ik}$$
$$\sum_j a_{ij}a_{kj}=\delta_{ik} \tag{8.14}$$

And the determinant of the matrix above is 1. For example rotation by an angle φ about the z axis is represented by the matrix

$$\begin{pmatrix}\cos\phi&\sin\phi&0\\-\sin\phi&\cos\phi&0\\0&0&1\end{pmatrix}$$

For $\phi=\frac{\pi}{2}$, this transformation becomes

$$\begin{pmatrix}0&1&0\\-1&0&0\\0&0&1\end{pmatrix}\begin{pmatrix}x\\y\\z\end{pmatrix}=\begin{pmatrix}y\\-x\\z\end{pmatrix} \tag{8.15}$$

This can easily be written as the transformation

$$x\ y\ z \rightarrow x'\ y'\ z' = \left(y\ \bar{x}\ z\right) \quad i.e.\ x' = y, y' = -x, z' = z$$

where $\bar{x}$ denotes $-x$.

Operating the same transformation twice, $x\,yz \rightarrow \bar{x}\,\bar{y}\,z$. Now, $\chi_{ij}^{(1)}$ transform like the product $x_i x_j$ of coordinates.

Thus, on transformation of axes by $x\ y\ z \rightarrow y\bar{x}\ z$ $\chi_{XY}^{(1)} \rightarrow -\chi_{XY}^{(1)}$ but since this coordinate transformation leaves the crystal unchanged $\chi_{XY}^{(1)}$ also must remain unchanged, as it is a property of the crystal.

$$\therefore \chi_{XY}^{(1)} = -\chi_{XY}^{(1)} \Rightarrow \chi_{XY}^{(1)} = 0 = \chi_{YX}^{(1)}$$

Similarly, one can show that $\chi_{YZ}^{(1)} = -\chi_{ZY}^{(1)} = 0 = \chi_{ZX}^{(1)} = \chi_{XZ}^{(1)}$.

Rotation by $\frac{\pi}{2}$ about the X, Y and Z axes leaves a simple cubic crystal invariant. For such crystal therefore $\chi^{(1)}$ is a diagonal tensor.

Another symmetry operation for the cubic crystal is a rotation by $\frac{2\pi}{3}$ about the body diagonal. The corresponding transformation matrix is (easiest to see this by looking at a cube along the body diagonal) $\left(x\ y\ z\right) \rightarrow \left(y\ z\ x\right)$

Similarly rotation by $\frac{4\pi}{3}$ about the body diagonal the body diagonal

$$\left(x\ y\ z\right) \rightarrow \left(z\ x\ y\right)$$

Using, these two relations we get

$$\chi_{XX}^{(1)} = \chi_{YY}^{(1)} = \chi_{ZZ}^{(1)}$$

Thus for the cubic crystal $\overleftrightarrow{\chi}^{(1)}$ is a diagonal tensor

$$\overleftrightarrow{\chi}^{(1)} = \overleftrightarrow{\chi}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Or $$\chi_{ij}^{(1)} = \chi^{(1)}(\omega)\delta_{ij}$$

Thus we say that a cubic crystal is optically isotropic in the electric dipole approximation.

This illustration was for a simple cubic crystal

However, as described by example (3) for zinc–blende structure all cubic crystal have at least the symmetry of tetrahedron and are optically isotropic in the electric dipole approximation.

Example 2:

If inversion is an element of symmetry for a medium

$$a_{ij} = (-1)\,\delta_{ij}$$

$$\therefore \chi_{\mu\alpha_1\ldots\alpha_n}^{(n)} = (-1)^{n+1}\,\chi_{\mu\alpha_1\ldots\alpha_n}^{(n)}$$

$$\Rightarrow \overleftrightarrow{\chi}^{(n)} = 0 \text{ for all even n.}$$

All even order electric-dipole susceptibilities vanish for inversion symmetric media. Near the surface, however, there is no inversion symmetry. This has the consequence that second harmonic generation from inversion symmetric media is a very sensitive probe of the medium near the surface. This is now a very useful tool for research in surface physics and chemistry. [see e.g., C S Tian and Y. R Shen, Smface Sc. Ref. 69,105(2014)]

Example 3:

The unit cell of a zinc blende crystal shown in Figure 8.1 can be taken as a tetrahedron with its centre as the origin and the 4 vertices at

$(a/4)(-1,-1,-1)$; $(a/4)(1,1,-1)$; $(a/4)(-1,1,1)$ and $(a/4)(1,-1,1)$.

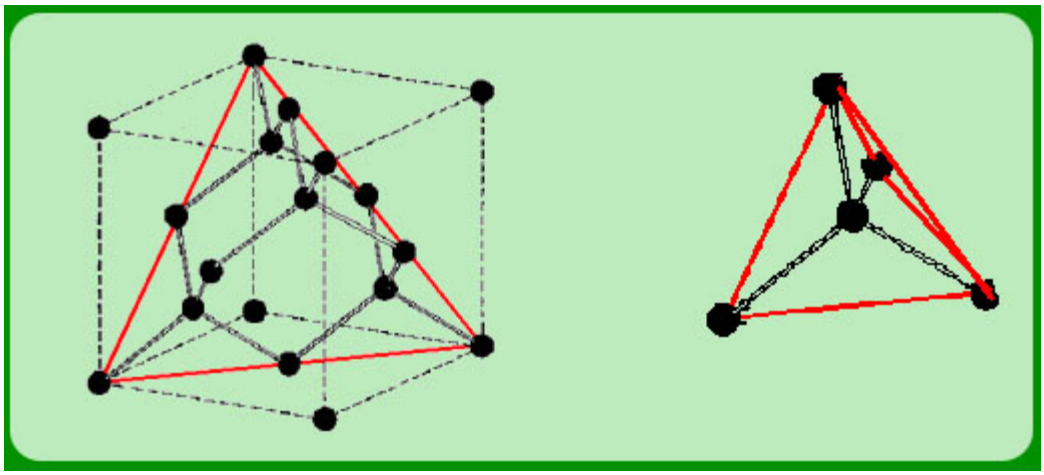

Figure 8.1 The zinc-blende structure, commonly found for compound semiconductors like GaAs and ZnSe

One can easily verify that the structure remains invariant under the symmetry operations given by $x, y, z \rightarrow x', y', z' =$

X	Y	Z
-X	-Y	Z
X	-Y	-Z
-X	Y	-Z
Y	-X	-Z
-Y	X	-Z
-X	Z	-Y
-X	-Z	Y
-Z	-Y	X
Z	-Y	-X
-Y	-X	Z
-Z	Y	-X
X	-Z	-Y
Y	X	Z
Z	Y	X
X	Z	Y
Z	X	Y
Y	Z	X
Z	-X	-Y
-Y	-Z	X
-Z	-X	Y
-Y	Z	-X
-Z	X	-Y
Y	-Z	-X

Since all operations used in example 1 are allowed symmetry operations, it follows that the linear susceptibility tensor is diagonal with all diagonal elements equal.

$$x\,y\,z \to \bar{x}\,\bar{y}\,z \text{ and } x\,y\,z \to \bar{x}\,y\,\bar{z} \text{ and } x\,y\,z \to x\,\bar{y}\,\bar{z}$$

are allowed symmetry operations implies that all components of $\vec{\vec{\chi}}^{(2)}$ tensor which have two or three identical are zero. So all indices have to be different.

The presence of symmetry operations $x\,y\,z \to y\,z\,x$ and $x\,y\,z \to z\,x\,y$ implies that all nonzero elements of $\vec{\vec{\chi}}^{(2)}$ tensor have to be equal.

Tables showing the symmetry imposed structure of first, second and third order susceptibilities are given in several standard texts such as those by Boyd and by Powers. Some of the more important ones are given in the Problems.

RECAP:

In this lecture we have learned about the

- We have defined nonlinear susceptibility tensors as Fourier transforms of Response Functions.
- Polarization at a given time may depend on fields at all previous times, so it is not just a function of the field at that time only.
- The n^{th} order susceptibility tensor $\chi^{(n)}_{\mu\alpha_1,\ldots\alpha_n}(-(\omega_1+\omega_2\ldots+\omega_n),\omega_1,\omega_2,..\omega_n)$ describes generation of a polarization oscillating at frequency $(\omega_1+\omega_2\ldots+\omega_n)$ polarized in the direction μ because of the combined action of fields $\vec{E}(\omega_1)$ polarized along direction α_1, $\vec{E}(\omega_2)$ polarized along α_2,... and $\vec{E}(\omega_n)$ polarized along α_n.