NLO Lecture 3: Nonlinear Optical Susceptibilities

2 Nonlinear optical susceptibilities

2.2 Classical model for nonlinear optical susceptibility

2.2.1 Linear susceptibility

2.2.2 Nonlinear susceptibility

2.3 Miller's d-Coefficient

2.4 Properties of the nonlinear susceptibilities

2.4.1 Physical fields are real

2.4.2 Permutation symmetry

2.4.3 Symmetry for lossless media

2.4.4 Kleinman's symmetry

2.4.5 Neumann's principle

2.2 Classical model for nonlinear optical susceptibility

$$F(x) = -\frac{\partial V(x)}{\partial x} = -m\omega_0^2 x \left(1 + \frac{x}{a} + \frac{x^2}{b^2}\right) \tag{2.13}$$

$$= -m\omega_0^2 x - m\beta_2 x^2 - m\beta_3 x^3 \tag{2.14}$$

$$\text{with } \beta_2 = \frac{\omega_0^2}{a} \text{ and } \beta_3 = \frac{\omega_0^2}{b^2} \,. \tag{2.15}$$

$$m\frac{d^2x}{dt^2} = -2\frac{\omega_0}{Q}m\frac{dx}{dt} + F(x) - e_0 E(t)$$

$$\frac{d^2x}{dt^2} + 2\frac{\omega_0}{Q}\frac{dx}{dt} + \omega_0^2 x + \beta_2 x^2 + \beta_3 x^3 = -\frac{e_0}{m}E(t). \tag{2.16}$$

Perturbation Solution:

$|\beta_2 x + \beta_3 x^2| \ll \omega_0^2$ $\quad x(t) = x_0(t) + \epsilon x_1(t) + \epsilon^2 x_2(t) + \ldots$

Zero order solution

$$(0) \quad : \quad \left(\frac{d^2}{dt^2} + 2\frac{\omega_0}{Q}\frac{d}{dt} + \omega_0^2\right) x_0(t) = -\frac{e_0}{m} E(t) \tag{2.18}$$

$$(1) \quad : \quad \left(\frac{d^2}{dt^2} + 2\frac{\omega_0}{Q}\frac{d}{dt} + \omega_0^2\right) x_1(t) = -\beta_2 \left(x_0\right)^2 - \beta_3 \left(x_0\right)^3 \tag{2.19}$$

$$(2) \quad : \quad \left(\frac{d^2}{dt^2} + 2\frac{\omega_0}{Q}\frac{d}{dt} + \omega_0^2\right) x_2(t) = -2\beta_2 x_0 x_1 - 3\beta_3 x_0^2 x_1 \tag{2.20}$$

2.2.1 Linear Susceptibility

$$x_0(t) = \frac{1}{2}\left(\hat{x}_0(\omega)e^{j\omega t} + c.c.\right)$$

$$P^{(1)}(t) = \frac{1}{2}\left(\hat{P}^{(1)}(\omega)e^{j\omega t} + c.c.\right) = -Ne_0 \cdot x_0(t)$$

in case of a time-varying field with amplitude $E(\omega)$ and frequency ω

$$E(t) = \frac{1}{2}\left(\hat{E}(\omega)e^{j\omega t} + c.c.\right) \tag{2.21}$$

Eq. (2.18) with $x_0(t)$ or its Fourier transforms

$$(0) \quad : \quad \hat{x}_0(\omega) = \frac{-e_0}{m\left(\omega_0^2 - \omega^2 + j\frac{2}{Q}\omega_0\omega\right)}\hat{E}(\omega),$$

$$(1) \quad : \quad \hat{P}^{(1)}(\omega) = \frac{Ne_0^2}{m\left(\omega_0^2 - \omega^2 + j\frac{2}{Q}\omega_0\omega\right)}\hat{E}(\omega) = \varepsilon_0\chi^{(1)}\hat{E}(\omega).$$

Therefore, the linear susceptibility is

$\omega_P = \sqrt{\frac{Ne_0^2}{m\varepsilon_0}}$ is the plasma frequency

$$\chi^{(1)}(\omega) = \frac{Ne_0^2}{m\varepsilon_0\left(\omega_0^2 - \omega^2 + j\frac{2}{Q}\omega_0\omega\right)} = \frac{\omega_P^2}{\left(\omega_0^2 - \omega^2 + j\frac{2}{Q}\omega_0\omega\right)} \tag{2.22}$$

Real and Imaginary Part of the Susceptibility

$$\chi^{(1)} = \chi^{(1)\prime} + j\chi^{(1)\prime\prime} \tag{2.23}$$

$$\chi^{(1)\prime} = \frac{\omega_P^2}{\omega_0^2} \frac{\left(1 - \frac{\omega^2}{\omega_0^2}\right)}{\left[\left(1 - \frac{\omega^2}{\omega_0^2}\right)^2 + \frac{4}{Q^2}\frac{\omega^2}{\omega_0^2}\right]} \tag{2.24}$$

$$\chi^{(1)\prime\prime} = -\frac{\omega_P^2}{\omega_0^2} \frac{\frac{2}{Q}\frac{\omega}{\omega_0}}{\left[\left(1 - \frac{\omega^2}{\omega_0^2}\right)^2 + \frac{4}{Q^2}\frac{\omega^2}{\omega_0^2}\right]} \tag{2.25}$$

Real and Imaginary Part of the Susceptibility

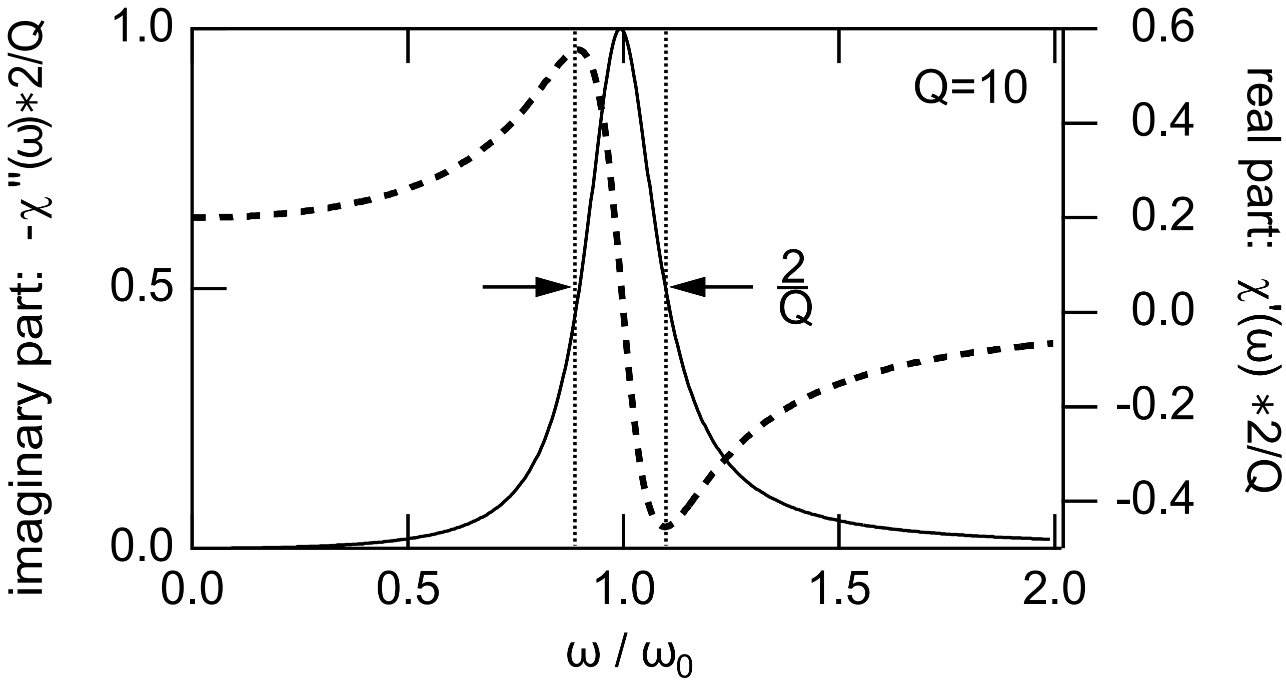

Figure 2.1: Susceptibility arising from the linear harmonic oscillator model for the electron cloud surrounding an atomic core.

Real and Imaginary Part of the Susceptibility

$$
\begin{aligned}
\chi^{(1)}(\omega) &= \frac{\omega_P^2}{\left(\omega_0^2 - \omega^2 + j\frac{2}{Q}\omega_0\omega\right)} && (2.26)\\
&= \frac{\omega_P^2}{2j\omega_0'}\left[\frac{1}{\left(\frac{1}{Q} + j\left(\omega - \omega_0'\right)\right)} - \frac{1}{\left(\frac{1}{Q} + j\left(\omega + \omega_0'\right)\right)}\right] && (2.27)\\
&\approx \frac{\omega_P^2}{2j\omega_0}\left[\frac{1}{\left(\frac{1}{Q} + j\left(\omega - \omega_0\right)\right)} - \frac{1}{\left(\frac{1}{Q} + j\left(\omega + \omega_0\right)\right)}\right] && (2.28)\\
&\approx \frac{\omega_P^2}{2j\omega_0}\frac{1}{\left(\frac{1}{Q} + j\left(\omega - \omega_0\right)\right)}, \text{für } \omega \quad \text{um } +\omega_0. && (2.29)
\end{aligned}
$$

where $\omega_0' = \omega_0\sqrt{1 - \frac{1}{Q^2}}$ is the exact resonance frequency of the damped harmonic oscillator.

2.2.2. Nonlinear Susceptibility

$$\begin{aligned} x_1(t) &= \hat{x}_1(0) + \frac{1}{2}\left(\hat{x}_1(\omega)e^{j\omega t} + c.c.\right) \\ &\quad + \frac{1}{2}\left(\hat{x}_1(2\omega)e^{j2\omega t} + c.c.\right) + \frac{1}{2}\left(\hat{x}_1(3\omega)e^{j3\omega t} + c.c.\right) \end{aligned}$$

With the susceptibility $\chi^{(1)}(\omega)$, which is up to the prefactor$-Ne_0/\varepsilon_0$ equal to the impulse repsonse of Eq.(2.18), we can find the first order amplitudes of all the different frequency components according to

$$\hat{x}_1(0) = -\beta_2 \frac{1}{\omega_0^2}\left|\left(\frac{-e_0}{m\left(\omega_0^2 - \omega^2 + j\frac{2}{Q}\omega_0\omega\right)}\right)\right|^2 \left|\hat{E}(\omega)\right|^2 \quad (2.30)$$

$$= -\beta_2 \frac{\chi^{(1)}(0)}{\omega_P^2}\left(-\frac{Ne_0}{\varepsilon_0}\right)^{-2} \left|\chi^{(1)}(\omega)\right|^2 \left|\hat{E}(\omega)\right|^2, \quad (2.31)$$

$$\hat{x}_1(2\omega) = \frac{-\beta_2}{2}\frac{\chi^{(1)}(2\omega)}{\omega_P^2}\left(-\frac{Ne_0}{\varepsilon_0}\right)^{-2} \chi^{(1)}(\omega)^2 \hat{E}(\omega)^2, \quad (2.32)$$

$$\hat{x}_1(\omega) = \frac{-3\beta_3}{4}\frac{\chi^{(1)}(\omega)}{\omega_P^2}\left(-\frac{Ne_0}{\varepsilon_0}\right)^{-3} \left|\chi^{(1)}(\omega)\right|^2 \left(\chi^{(1)}(\omega)\right) \quad (2.33)$$

$$\times \left|\hat{E}(\omega)\right|^2 \hat{E}(\omega), \quad (2.34)$$

$$\hat{x}_1(3\omega) = \frac{-\beta_3}{4}\frac{\chi^{(1)}(3\omega)}{\omega_P^2}\left(-\frac{Ne_0}{\varepsilon_0}\right)^{-3} \chi^{(1)}(\omega)^3 \hat{E}(\omega)^3. \quad (2.35)$$

Susceptibilities

$$\chi^{(2)}(0;\omega,-\omega) = -\frac{m\beta_2}{e_0}\left(-\frac{Ne_0}{\varepsilon_0}\right)^{-2}\chi^{(1)}(0)\left|\chi^{(1)}(\omega)\right|^2, \quad (2.36)$$

$$\chi^{(2)}(2\omega;\omega,\omega) = \frac{-m\beta_2}{2e_0}\left(-\frac{Ne_0}{\varepsilon_0}\right)^{-2}\chi^{(1)}(2\omega)\chi^{(1)}(\omega)^2, \quad (2.37)$$

$$\chi^{(3)}(\omega;\omega,-\omega,\omega) = \frac{-3m\beta_3}{4e_0}\left(-\frac{Ne_0}{\varepsilon_0}\right)^{-3}\left|\chi^{(1)}(\omega)\right|^2\left(\chi^{(1)}(\omega)\right)^2, \quad (2.38)$$

$$\chi^{(3)}(3\omega;\omega,\omega,\omega) = \frac{-m\beta_3}{4e_0}\left(-\frac{Ne_0}{\varepsilon_0}\right)^{-3}\chi^{(1)}(3\omega)\chi^{(1)}(\omega)^3. \quad (2.39)$$

2.3 Miller's δ-Coefficient

$$\delta_{ijk} = \frac{\chi^{(2)}_{ijk}(2\omega:\omega,\omega)}{\chi^{(1)}_{ii}(2\omega)\chi^{(1)}_{jj}(\omega)\chi^{(1)}_{kk}(\omega)} = \frac{\chi^{(2)}_{ijk}(2\omega:\omega,\omega)}{\left(n^2(2\omega)-1\right)\left(n^2(\omega)-1\right)^2}$$

$$= \frac{-m\beta_2}{2}\frac{\varepsilon_0^2}{N^2e_0^3}.$$

Experimentally one finds, that these coefficients do not depend strongly on the material for inorganic materials. We assume that the deviation x (see Eq. (2.13)) is the lattice constant with $a \approx (N)^{-1/3}$, then we obtain with Eq. (2.15) for the Miller coefficient

$$|\delta_{ijk}| \approx \frac{m\omega_0^2}{2}\frac{\varepsilon_0^2}{N^{5/3}e_0^3}.$$

$$\lambda_0 = 200\ \text{nm},\ \omega_0 = 3\pi\cdot\ \text{fs}^{-1} \qquad a = 3\cdot 10^{-10}\ \text{m}^{-1}$$

$$|\delta_{ijk}| \approx 3.7\cdot 10^{-12}\frac{V}{m}$$

2.4 Properties of the nonlinear susceptibilities

2.4.1 Physical fields are real

$$\chi^{(n)}_{ij...s}(\omega_b; \omega_1, ..., \omega_n)^* = \chi^{(n)}_{ij...s}(-\omega_b; -\omega_1, ..., -\omega_n) \quad (2.40)$$

$$\omega_b = \sum_{i=1}^{n} \omega_i \quad (2.41)$$

2.4.2 Permutation symmetry

numbering 1 to *n* arbitrary → use symmetric definition

$$\chi^{(n)}_{i...j...o...s}(\omega_b; ...\omega_{l,...}\omega_k...., \omega_n) = \chi^{(n)}_{i...o...j...s}(\omega_b; ...\omega_{k,...}\omega_l...., \omega_n). \quad (2.42)$$

2.4.3 Symmetry for lossless media

two additional symmetries:

- imaginary part of the susceptibility describes loss and gain
  $\rightarrow$ susceptibilities of lossless media are real
- complete permutation symmetry independent, if the frequency is an input or output frequency

$$\chi^{(n)}_{i...j...o...s}(\omega_b; ...\omega_{l,...}\omega_k ..., \omega_n) = \chi^{(n)}_{j...i...o...s}(-\omega_l; ... - \omega_{b,...}\omega_k ..., \omega_n), \qquad (2.43)$$

In combination with first symmetry (Eq. (2.40))

$$\chi^{(n)}_{i...j...o...s}(\omega_b; ...\omega_{l,...}\omega_k ..., \omega_n) = \chi^{(n)}_{j...i...o...s}(\omega_l; ...\omega_{b,...} - \omega_k ..., -\omega_n). \qquad (2.44)$$

This implies that in the lossless case, the susceptibilities for sum- and difference-frequency generation are equal if the frequencies and polarizations involved are chosen accordingly. For the classical model treated before, this is immediately clear. Furthermore, it can also generally be proven by a quantum mechanical derivation of the susceptibility or with the help of the energy conservation [3].

2.4.4 Kleinman's symmetry

low-frequency range: medium lossless,
susceptibilities essentially **independent of wavelength**
$\rightarrow$ indices of susceptibilities can arbitrarily be permuted,
nonlinearity responds instantaneously to the electric field

$$\begin{aligned}\chi^{(n)}_{i\ldots j\ldots o\ldots s}(\omega_b; \ldots\omega_{l,\ldots}\omega_k\ldots, \omega_n) &= \chi^{(n)}_{j\ldots i\ldots o\ldots s}(\omega_b; \ldots\omega_{l,\ldots}\omega_k\ldots, \omega_n) \\ &= \chi^{(n)}_{j\ldots i\ldots o\ldots s} = \text{const.}\end{aligned} \quad (2.45)$$

$$P_i^{(2)}(t) = \sum_{jk} \chi^{(2)}_{ijk} E_j(t) E_k(t). \quad (2.46)$$

2.4.5 Neumann's principle

coordinate transformations (inversion, mirror image and rotation) **T** of field and polarization vectors **E** and **P**

$$\begin{pmatrix} E_x' \\ E_y' \\ E_z' \end{pmatrix} = \begin{pmatrix} T_{x'x} & T_{x'y} & T_{x'z} \\ T_{y'x} & T_{y'y} & T_{y'z} \\ T_{z'x} & T_{z'y} & T_{z'z} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix} \tag{2.47}$$

$$\mathbf{E}' = \mathbf{T} \cdot \mathbf{E} \tag{2.48}$$

$$\mathbf{E} = \mathbf{T}^{-1} \cdot \mathbf{E}' \tag{2.49}$$

inversion, mirror image and rotation are orthogonal transformations: $\mathbf{T}^T = \mathbf{T}^{-1}$

$$\mathbf{E} = \mathbf{T}^T \cdot \mathbf{E}' \tag{2.50}$$

employing Einstein’s summation convention

$$E_i = (T_{ii'})^T E_{i'} = T_{i'i} E_{i'} \tag{2.51}$$

$$P_i = T_{i'i} P_{i'} \tag{2.52}$$

relations in the two coordinate systems

$$P_i^{(n)} = \varepsilon_0 \chi_{ij\ldots s}^{(n)} E_j \cdots E_s, \tag{2.53}$$

$$P_{i'}^{(n)} = \varepsilon_0 \chi_{i'j'\ldots s'}^{(n)} E_{j'} \cdots E_{s'}, \tag{2.54}$$

Then

$$T_{i'i} P_i^{(n)} = P_{i'}^{(n)} = \varepsilon_0 T_{i'i} \chi_{ij\ldots s}^{(n)} T_{j'j} E_{j'} T_{k'k} E_{k'} \cdots T_{s's} E_{s'} \tag{2.55}$$

$$\chi_{i'j'\ldots s'}^{(n)} = T_{i'i} T_{j'j} \cdots T_{s's} \chi_{ij\ldots s}^{(n)} \tag{2.56}$$

→ **nonlinear susceptibilities are tensors**

transformations, that do not change the physical reference between the fields and media, leave the susceptibilities invariant.

The **32 crystal classes**, that can be derived from the **7 crystal systems**, are characterized by being **invariant under a point group**. I.e., the susceptibility tensor of materials, belonging to a certain crystal class, must be invariant under the corresponding point group (**Neumann’s principle**).

Example: let's consider inversion $T_{i'i} = (-1)\delta_{i'i}$

susceptibility tensor of the inverted medium

$$\chi^{(n)}_{i'j'\ldots s'} = (-1)^{n+1}\chi^{(n)}_{ij\ldots s} \qquad (2.57)$$

If the medium is invariant under inversion, it follows for *n*=even

$$\chi^{(n)}_{ij\ldots s} = (-1)^{n+1}\chi^{(n)}_{ij\ldots s} = 0 \qquad (2.58)$$

i.e., in an inversion symmetric medium, the susceptibility tensors of even orders vanish
(no linear electro-optic effect, no SHG)

Of the 32 crystal classes, already 11 possess inversion symmetry. Remaining 21 non-centrosymmetric crystal classes, the number of nonvanishing tensor elements $\chi^{(2)}_{ijk}$ further reduce because of other symmetries. The symmetry properties of $\chi^{(2)}_{ijk}$ are the same as those of the piezo-electric tensor.

If the even nonlinear optical processes are forbidden by symmetry (e.g., in media such as glasses, gases, fluids), processes of third order are the dominating nonlinearity. The existing inversion symmetry also reduces the non-vanishing susceptibility tensor elements of third order $\chi_{ijkl}^{(3)}$.

2.5 The reduced susceptibility tensor of second order

second-order susceptibilities are expressed in terms of nonlinear coefficients $d_{ijk} = \frac{1}{2}\chi^{(2)}_{ijk}$

$$\hat{P}_i^{(2)}(\omega_n + \omega_m) = 2\varepsilon_0 \sum_{jk} d_{ijk}(\omega_n + \omega_m : \omega_n, \omega_m)\hat{E}_j(\omega_n)\hat{E}_k(\omega_m). \qquad (2.59)$$

If Kleinmann symmetry condition is valid (or for SHG), the nonlinear coefficients can be formulated in reduced form $d_{ijk} = d_{ikj} = d_{il}$, i.e., in these cases the indices *j* and *k* can be permuted.

$$[jk] = \begin{bmatrix} 11 & 12 & 13 \\ 21 & 22 & 23 \\ 31 & 32 & 33 \end{bmatrix} = [l] = \begin{bmatrix} 1 & 6 & 5 \\ 6 & 2 & 4 \\ 5 & 4 & 3 \end{bmatrix}. \qquad (2.60)$$

For SHG

$$\begin{bmatrix} P_x(2\omega) \\ P_y(2\omega) \\ P_z(2\omega) \end{bmatrix} = \varepsilon_0 \begin{bmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{bmatrix} \cdot \begin{bmatrix} E_x(\omega)^2 \\ E_y(\omega)^2 \\ E_z(\omega)^2 \\ 2E_y(\omega)E_z(\omega) \\ 2E_x(\omega)E_z(\omega) \\ 2E_x(\omega)E_y(\omega) \end{bmatrix}. \qquad (2.61)$$