Nonlinear Optics Study CH-1

Boyd, R. W. *Nonlinear optics* (4th ed.)

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1.1 Introduction to Nonlinear Optics

Introduction

- ***Nonlinear Optics***
  - The study of phenomena that occur as a consequence of the modification of the optical properties of a material system by the presence of light
  - Laser light is sufficiently intense to modify the optical properties of a material system

- ***Meaning of "Nonlinear"***
  - When the response of a material system to an applied optical field depends in a nonlinear manner on the strength of the applied optical system

- ***In order to describe more precisely what we mean by an optical nonlinearity,***

$$\tilde{P}(t) = \epsilon_0 \chi^{(1)} \tilde{E}(t)$$

  - Polarization $\tilde{P}(t)$ (the dipole moment per unit volume of a material system)
  - $\chi^{(1)}$: linear susceptibility
  - ϵ_0 : permittivity of free space

Optical Response for Nonlinear Optics

- ***As a power series in the field strength $\widetilde{E}(t)$***

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

  - $\chi^{(1)}, \chi^{(2)}$: second-rank tensor, third-rank tensor (the fields are vectors)

Dirac-delta function

$$\tilde{P}^{(1)}(t) = \epsilon_0 \int_0^\infty R^{(1)}(t-\tau)\tilde{E}(\tau)d\tau$$

- ***Assumption***
  - The polarization at time t depends only on the ***instantaneous*** value of the electric field strength
    - ◆ The medium must be lossless and dispersionless

Kramers-Kronig relations

  - In general, the nonlinear susceptibilities depend on the frequencies of the applied fields
    - ◆ Our assumption gives them to be constants

Optical Response for Nonlinear Optics

- ***Polarization : Act as the source of new components of the electromagnetic field***

$$\nabla^2 \tilde{E} - \frac{n^2}{c^2}\frac{\partial^2 \tilde{E}}{\partial t^2} = \frac{1}{\epsilon_0 c^2}\frac{\partial^2 \tilde{P}^{NL}}{\partial t^2}$$

- n : linear refractive index
- c : the speed of light in vacuum
- ***Inhomogeneous*** wave equation in which the polarization acts as a source term for the E-field

$$\frac{\partial^2 \tilde{P}^{NL}}{\partial t^2}$$

- A measure of the acceleration of the charges that constitute the medium
- Consistent with ***Larmor's theorem*** of Electromagnetism
  (accelerated charges generate electromagnetic radiation)

1.2 Descriptions of Nonlinear Optical Processes

Second Harmonic Generation

- ***Electric field strength of a laser beam in lossless medium***

$$\tilde{E}(t) = Ee^{-i\omega t} + c.c.$$

  - It is incident upon a crystal for which the second-order susceptibility is nonzero

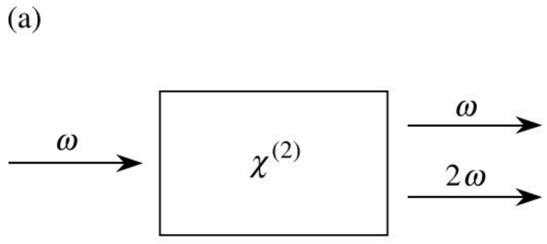


FIGURE 1.2.1: (a) Geometry of second-harmonic generation.
second-harmonic generation.

$$\tilde{P}^{(2)}(t) = \epsilon_0 \chi^{(2)} \tilde{E}^2(t)$$

$$\tilde{P}^{(2)}(t) = \boldsymbol{2\epsilon_0\chi^{(2)}EE^*} + \left(\boldsymbol{\epsilon_0\chi^{(2)}e^{-2i\omega t} + c.c}\right)$$

A contribution at zero frequency

A contribution at 2ω

- ***Driven Wave Equation***

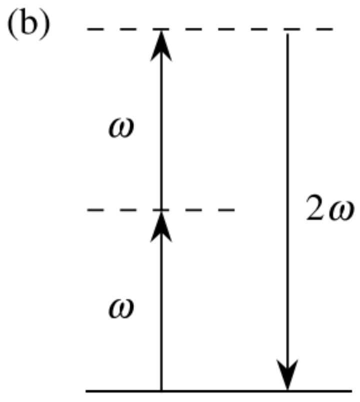
$$\nabla^2\tilde{E} - \frac{n^2}{c^2}\frac{\partial^2\tilde{E}}{\partial t^2} = \frac{1}{\epsilon_0 c^2}\frac{\partial^2\tilde{P}^{NL}}{\partial t^2}$$

  - Optical rectification : static electric field is created across the nonlinear crystal
  - The generation of radiation at 2ω

Second Harmonic Generation (cont.)

- ***Second-harmonic generation under experimental condition***
  - Nearly all of the power in the incident beam at ω is converted into radiation at the second-harmonic frequency 2ω
  - One common use of SHG is to convert the output of a fixed-frequency laser to a different spectral region
    - ◆ Nd:YAG laser (infrared @ $\lambda = 1.06\ \mu\text{m}$) → to convert (middile of visible spectrum @ $\lambda = 0.53\ \mu\text{m}$)

- ***Interaction in terms of the exchange of photons between the various frequencies of the field.***



(b) Energy-level diagram describing

- A single quantum-mechanical process
  - ◆ Two photon (ω) : destroyed, a photon (2ω) : simultaneously created
- Solid line : the atomic ground state
- Dashed line : virtual level
  - ◆ Not energy eigenlevels of the free atom
- Combined energy of the atom and of one or more photons of radiation

Sum and Difference-Frequency Generation

- ***Optical field incident upon a second-order nonlinear optical medium***

  - Two distinct frequency components

$$\tilde{E}(t) = E_1 e^{-i\omega_1 t} + E_2 e^{-i\omega_2 t} + E_1^* e^{i\omega_1 t} + E_2^* e^{i\omega_2 t} = E_1 e^{-i\omega_1 t} + E_2 e^{-i\omega_2 t} + c.c.$$

  - Nonlinear polarization

$$\tilde{P}^{(2)}(t) = \epsilon_0 \chi^{(2)} \tilde{E}^2(t)$$

$$= \epsilon_0 \chi^{(2)} \left(E_1 e^{-i\omega_1 t} + E_2 e^{-i\omega_2 t} + E_1^* e^{i\omega_1 t} + E_2^* e^{i\omega_2 t}\right)\left(E_1 e^{-i\omega_1 t} + E_2 e^{-i\omega_2 t} + E_1^* e^{i\omega_1 t} + E_2^* e^{i\omega_2 t}\right)$$

$$= \epsilon_0 \chi^{(2)} \left[E_1^2 e^{-2i\omega_1 t} + E_2^2 e^{-2i\omega_2 t} + 2E_1 E_2 e^{-i(\omega_1+\omega_2)t} + 2E_1 E_2^* e^{-i(\omega_2-\omega_1)t} + c.c.\right] + 2\epsilon_0 \chi^{(2)} [E_1 E_1^* + E_2 E_2^*]$$

  - The summation extends over positive and negative frequencies ω_n

$$\tilde{P}^{(2)}(t) = \sum_n P(\omega_n) e^{-i\omega_n t}$$

Sum and Difference-Frequency Generation (cont.)

- ***The complex amplitudes of the various frequencies of the nonlinear polarizations***

$$\tilde{P}^{(2)}(t) = \epsilon_0 \chi^{(2)} \left[E_1^2 e^{-2i\omega_1 t} + E_2^2 e^{-2i\omega_2 t} + 2E_1 E_2 e^{-i(\omega_1+\omega_2)t} + 2E_1 E_2^* e^{-i(\omega_2-\omega_1)t} + c.c. \right] + 2\epsilon_0 \chi^{(2)} [E_1 E_1^* + E_2 E_2^*]$$

- Labeling each terms with $\tilde{P}^{(2)}(t) = \sum_n P(\omega_n) e^{-i\omega_n t}$

SHG $\quad P(2\omega_1) = \epsilon_0 \chi^{(2)} E_1^2, \qquad P(2\omega_2) = \epsilon_0 \chi^{(2)} E_2^2 \quad$ SHG

SFG $\quad P(\omega_1 + \omega_2) = 2\epsilon_0 \chi^{(2)} E_1 E_2, \qquad P(\omega_1 - \omega_2) = 2\epsilon_0 \chi^{(2)} E_1 E_2^* \quad$ DFG

$P(0) = 2\epsilon_0 \chi^{(2)} [E_1 E_1^* + E_2 E_2^*] \quad$ OR

- Response at the negative frequency components

SHG $\quad P(-2\omega_1) = \epsilon_0 \chi^{(2)} E_1^{*2}, \qquad P(-2\omega_2) = \epsilon_0 \chi^{(2)} E_2^{*2} \quad$ SHG

SFG $\quad P(-\omega_1 - \omega_2) = 2\epsilon_0 \chi^{(2)} E_1^* E_2^*, \qquad P(\omega_2 - \omega_1) = 2\epsilon_0 \chi^{(2)} E_2 E_1^* \quad$ DFG

Phase-matching

- ***Introduction to phase-matching condition***

  - Four different nonzero frequency components

$$\text{SHG} \quad P(2\omega_1) = \epsilon_0 \chi^{(2)} E_1^2, \qquad P(2\omega_2) = \epsilon_0 \chi^{(2)} E_2^2 \quad \text{SHG}$$

$$\text{SFG} \quad P(\omega_1 + \omega_2) = 2\epsilon_0 \chi^{(2)} E_1 E_2, \qquad P(\omega_1 - \omega_2) = 2\epsilon_0 \chi^{(2)} E_1 E_2^* \quad \text{DFG}$$

$$P(0) = 2\epsilon_0 \chi^{(2)} [E_1 E_1^* + E_2 E_2^*] \quad \text{OR}$$

  - Typically, no more than one of four frequency components are present in the nonlinear polarization

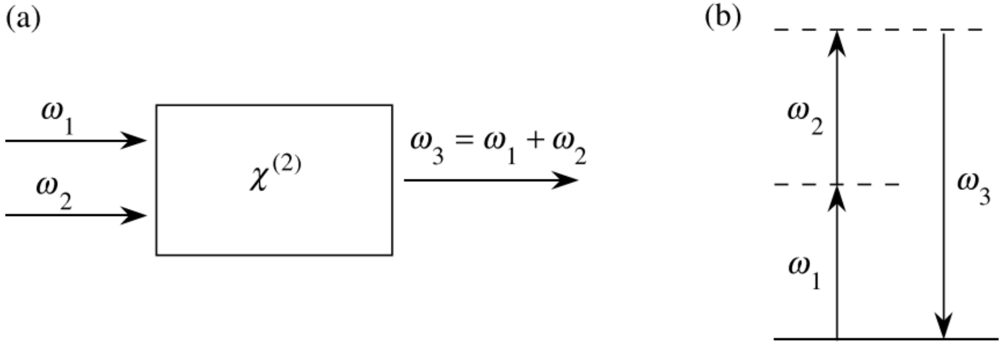
    - ◆ The nonlinear polarization can efficiently produce an output signal only if a certain ***phase-matching*** condition is satisfied

    - ◆ Usually this condition cannot be satisfied for more than one frequency component of the nonlinear polarization

  - Radiated frequencies are selected via **input polarization** and **crystal orientation**

Sum-Frequency Generation

- ***The process of SFG***



$$P(2\omega_1) = \epsilon_0 \chi^{(2)} E_1^2$$

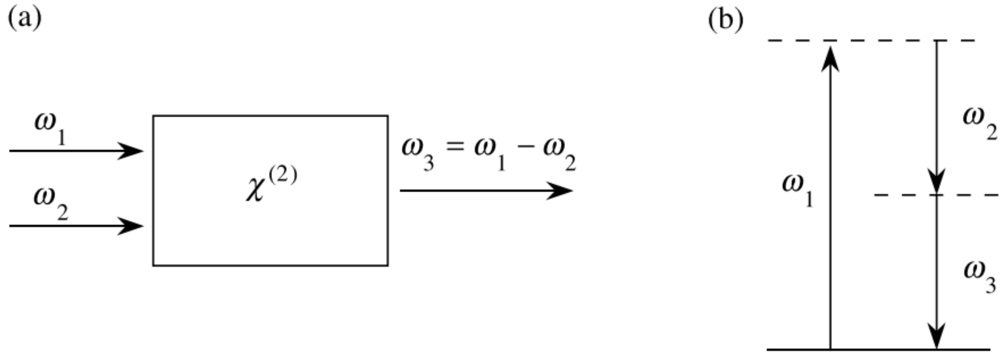
  - SFG is analogous to that of SHG, except that in SFG the two input waves are at different frequencies

- ***Application of SFG***

  - To produce : tunable radiation @ ultraviolet region
  - Choosing the input waves : fixed frequency laser and frequency-tunable laser @ visible region

Difference-Frequency Generation

- ***The process of DFG***



$$P(\omega_2 - \omega_1) = 2\epsilon_0 \chi^{(2)} E_1 E_2^*$$

- ***Application of DFG***

  - To produce : tunable radiation @ infrared region
  - By choosing the input waves : fixed frequency laser and frequency-tunable laser @ visible region

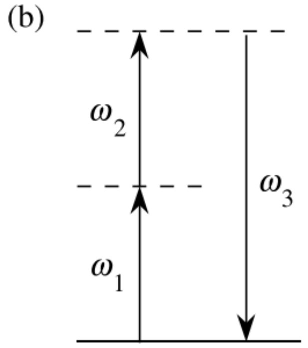
- DFG and SFG appear to be very similar processes

Optical parametric amplification

- ***Difference between SFG and DFG***
  - Conservation of energy

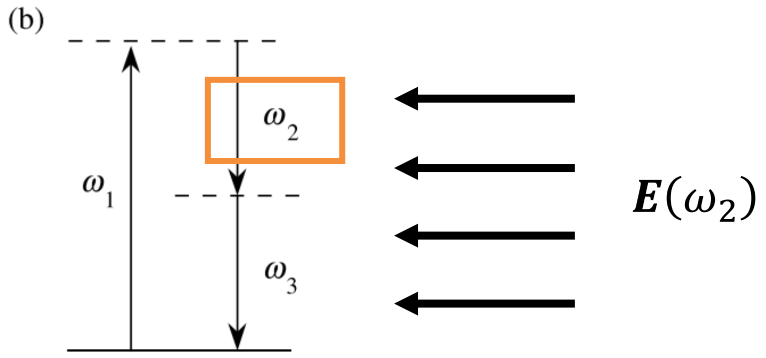
$$\omega_3 = \omega_2 + \omega_1$$

ω_2 : destroyed
ω_1 : destroyed

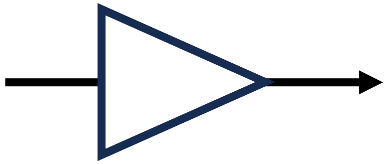


$$\omega_3 = \omega_2 - \omega_1$$

ω_2 : created
ω_1 : destroyed

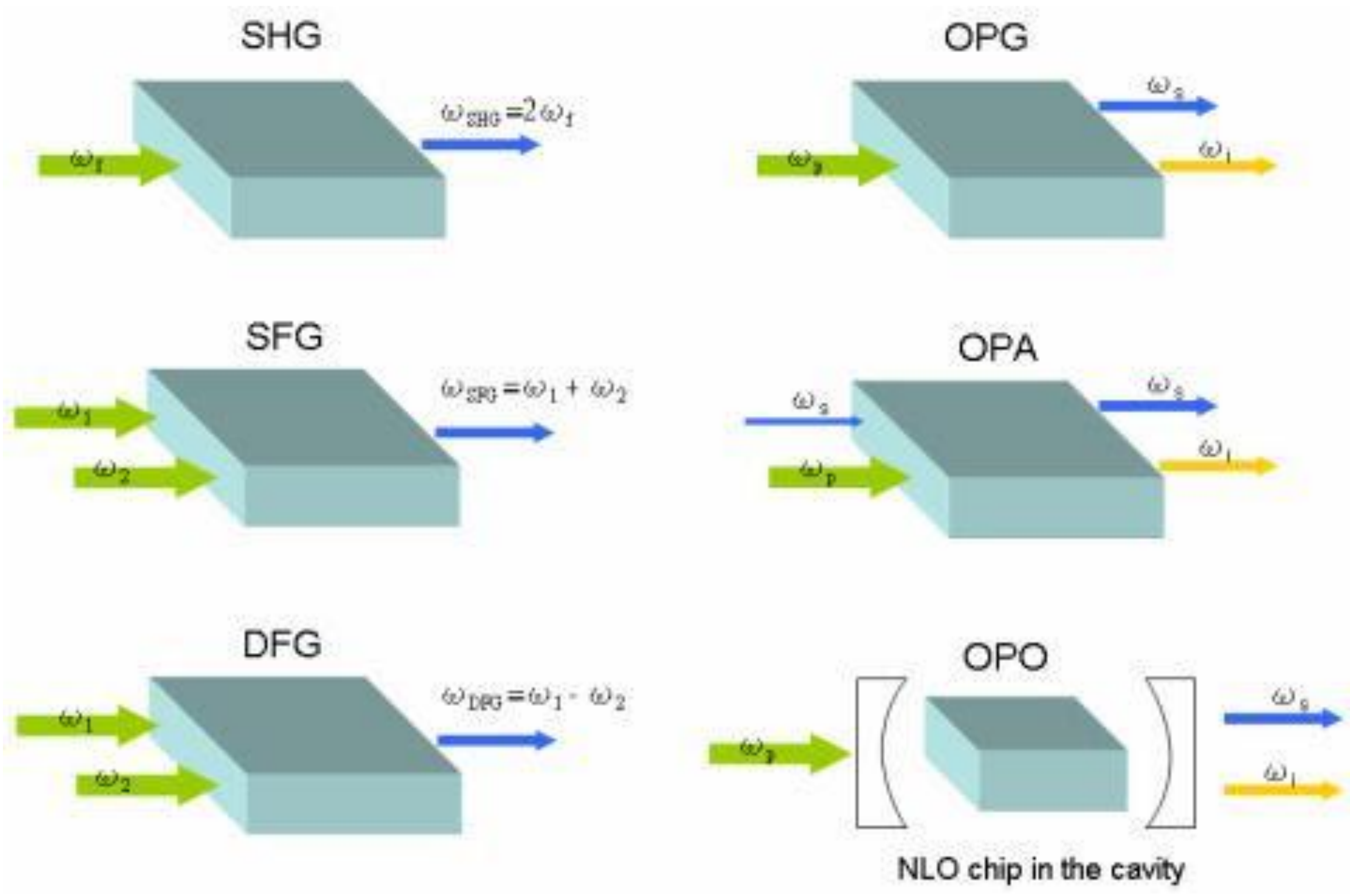


- ***DFG***
  - Photon (ω_3) : A photon (ω_1) is destroyed and a photon (ω_2) is created
    - ◆ The atom first absorbs a photon of frequency ω_1 and jumps to the highest virtual level
    - ◆ This level decays by a two-photon emission process that is ***stimulated*** by the ω_2 field
  - The lower-frequency input field is amplified by the process of DFG



Optical parametric amplification

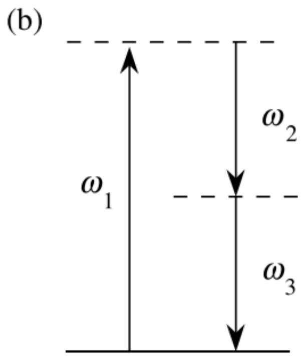
If the absence of the ω_2 field?


SHG
OPG
SFG
OPA
DFG
OPO
NLO chip in the cavity

Spontaneous Parametric Down Conversion

- ***The absence of E-field***

  - Even if the ω_2 field is not applied, two-photon emission can occur.



$$\omega_3 = \omega_2 - \omega_1$$

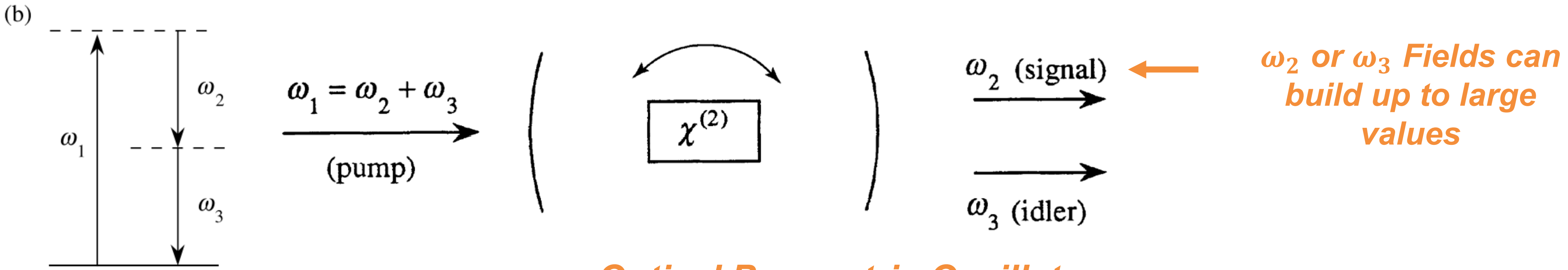
ω_2 : created
ω_1 : destroyed

  - In such a case, the generated fields are very much weaker
  - They are created by spontaneous two-photon emission from a virtual level

Spontaneous parametric down-conversion or Parametric fluorescence

Optical Parametric Oscillation

- ***In the process of DFG that the presence of radiation at ω_2 or ω_3 can stimulate the emission of photon***
  - If the nonlinear crystal used in this process is placed inside an optical resonator,



Optical Parametric Oscillator

  - A device is broadly tunable because of their extremely broad tuning range

$$\omega_1 = \omega_2 + \omega_3, \qquad \omega_2 < \omega_1$$

- ***In practical,***
  - Controlling output frequency of an optical parametric oscillator by adjusting phase-matching condition
  - The applied field frequency ω_1 : pump frequency
  - The desired output frequency : signal frequency ; The unwanted output frequency : idler frequency

Third-Order Nonlinear Optical Processes

- ***Third order contribution to the nonlinear polarization***

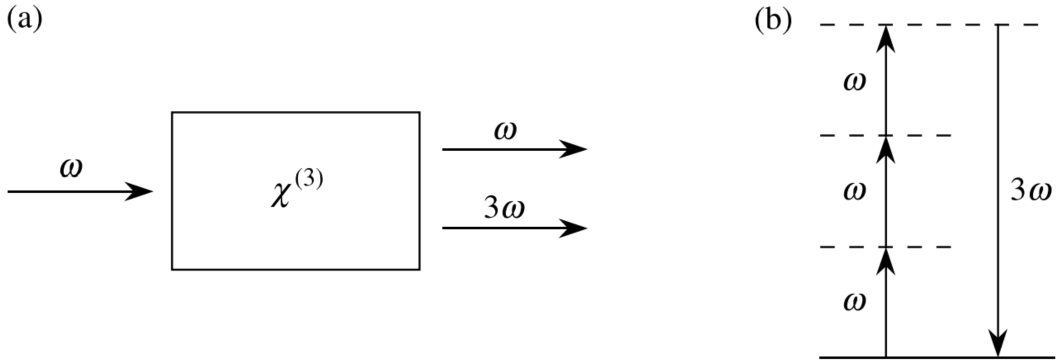
$$\tilde{P}^{(3)}(t) = \epsilon_0 \chi^{(3)} \tilde{E}(t)^3$$

  - Generally, the E-field is made up of several different frequency components
  - But it is very complicated, so we first consider monochromatic applied field

$$\tilde{E}(t) = \mathcal{E}\cos(\omega t)$$

$$\tilde{P}^{(3)}(t) = \frac{1}{4}\epsilon_0 \chi^{(3)} \mathcal{E}^3 \cos^3(3\omega t) + \frac{3}{4}\epsilon_0 \chi^{(3)} \mathcal{E}^3 \cos(\omega t)$$

- ***Third-harmonic generation***



- Three photons (ω) are destroyed
- One photon (3ω) is created

Intensity-Dependent Refractive Index

- ***Nonlinear contribution to the refractive index***

$$\tilde{P}^{(3)}(t) = \frac{1}{4}\epsilon_0\chi^{(3)}\mathcal{E}^3\cos^3(3\omega t) + \boldsymbol{\frac{3}{4}\epsilon_0\chi^{(3)}\mathcal{E}^3\cos(\omega t)}$$

- The refractive index in the presence of this type of nonlinearity

$$n = n_0 + n_2 I$$

$$n_2 = \frac{3}{4n_0^2\epsilon_0 c}\chi^{(3)}$$

Optical constant in lossless medium

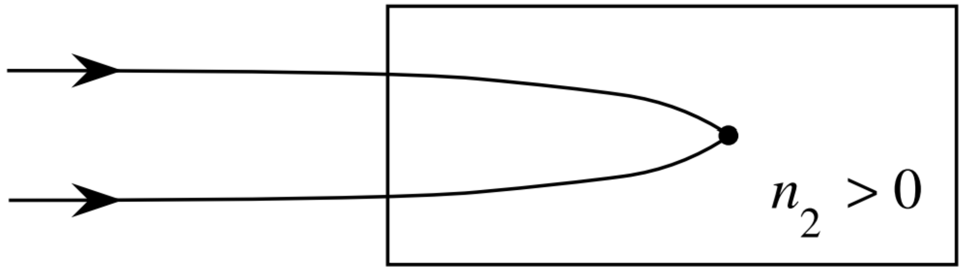
◆ n_0 : usual (linear or low-intensity) refractive index

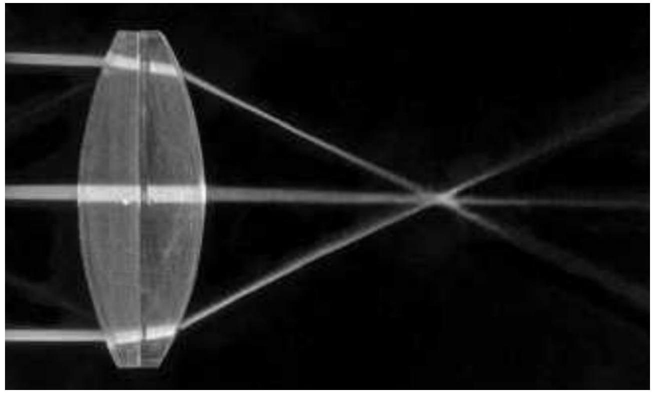
◆ n_0 $I = \frac{1}{2}n_0\epsilon_0 c\mathcal{E}^2$: the intensity of incident wave

Self Focusing

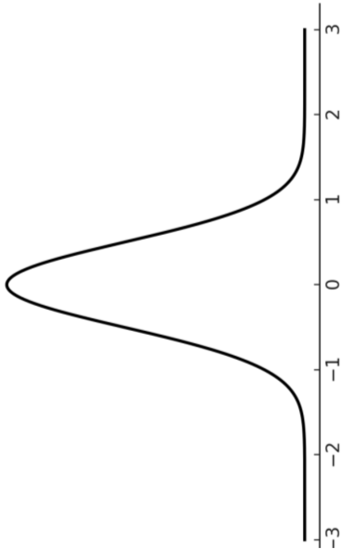
- ***If intensity-dependent refractive index is Self-Focusing***

the material effectively acts as a positive lens





$$n = n_0 + n_2 I$$



- The process can occur when a beam of light having a nonuniform transverse intensity distribution propagates through a material for which n_2 is positive

- The intensity at the focal spot of the self focused beam is usually sufficiently large to lead to optical damage of the material

Third-Order Interactions (General Case)

- ***Nonlinear polarization consists of three frequency components***

$$\tilde{P}^{(3)}(t) = \epsilon_0 \chi^{(3)} \tilde{E}(t)^3$$

$$\tilde{E}(t) = E_1 e^{-i\omega_1 t} + E_2 e^{-i\omega_2 t} + E_3 e^{-i\omega_3 t} + +c.c.$$

  - When calculating $\tilde{E}(t)^3$, we find 44 different frequency components (considering positive and negative frequencies)

$$\omega_1, \omega_2, \omega_3, 3\omega_1, 3\omega_2, 3\omega_3, (\omega_1 + \omega_2 + \omega_3), (\omega_1 + \omega_2 - \omega_3),$$
$$(\omega_1 + \omega_3 - \omega_2), (\omega_2 + \omega_3 - \omega_1), (2\omega_1 \pm \omega_2), (2\omega_1 \pm \omega_3), (2\omega_2 \pm \omega_1),$$
$$(2\omega_2 \pm \omega_3), (2\omega_3 \pm \omega_1), (2\omega_3 \pm \omega_2),$$

Third-Order Interactions (General Case)

- Again representing the nonlinear polarization $\tilde{P}^{(3)}(t) = \sum_n P(\omega_n)e^{-i\omega_n t}$

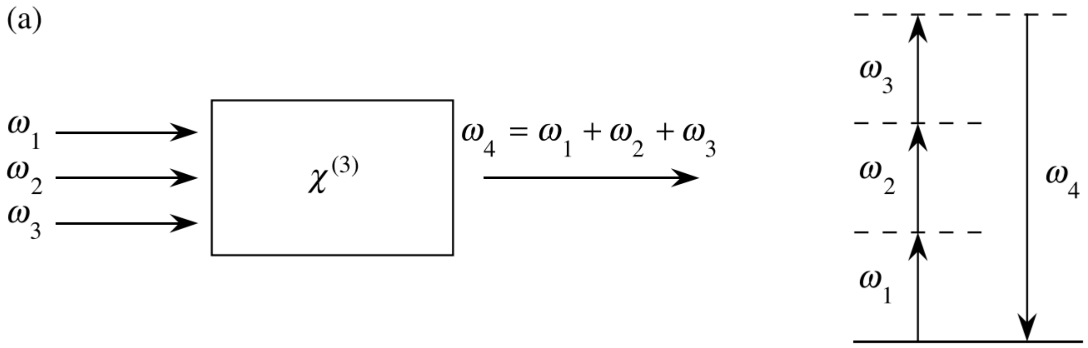
$$P(\omega_1) = \epsilon_0\chi^{(3)}\left(3E_1E_1^* + 6E_2E_2^* + 6E_3E_3^*\right)E_1,$$
$$P(\omega_2) = \epsilon_0\chi^{(3)}\left(6E_1E_1^* + 3E_2E_2^* + 6E_3E_3^*\right)E_2,$$
$$P(\omega_3) = \epsilon_0\chi^{(3)}\left(6E_1E_1^* + 6E_2E_2^* + 3E_3E_3^*\right)E_3,$$

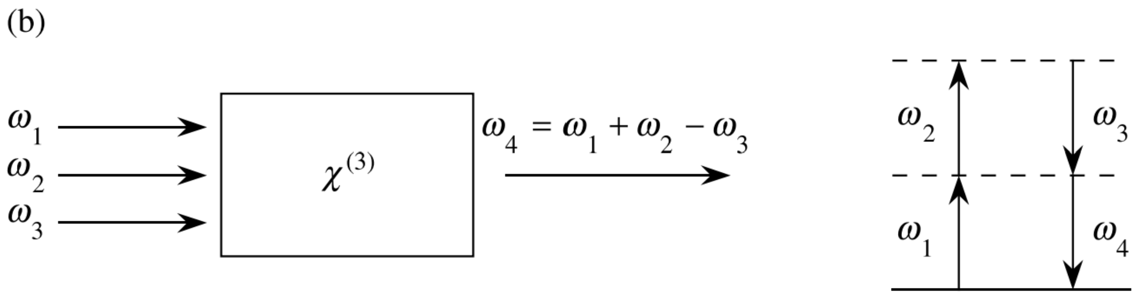
$$P(3\omega_1) = \epsilon_0\chi^{(3)}E_1^3, \qquad P(3\omega_2) = \epsilon_0\chi^{(3)}E_2^3, \qquad P(3\omega_3) = \epsilon_0\chi^{(3)}E_3^3,$$

$$\boxed{\begin{aligned} P(\omega_1+\omega_2+\omega_3) &= 6\epsilon_0\chi^{(3)}E_1E_2E_3, \\ P(\omega_1+\omega_2-\omega_3) &= 6\epsilon_0\chi^{(3)}E_1E_2E_3^*, \end{aligned}}$$
$$P(\omega_1+\omega_3-\omega_2) = 6\epsilon_0\chi^{(3)}E_1E_3E_2^*,$$
$$P(\omega_2+\omega_3-\omega_1) = 6\epsilon_0\chi^{(3)}E_2E_3E_1^*,$$

$$P(2\omega_1+\omega_2) = 3\epsilon_0\chi^{(3)}E_1^2E_2, \qquad P(2\omega_1+\omega_3) = 3\epsilon_0\chi^{(3)}E_1^2E_3,$$
$$P(2\omega_2+\omega_1) = 3\epsilon_0\chi^{(3)}E_2^2E_1, \qquad P(2\omega_2+\omega_3) = 3\epsilon_0\chi^{(3)}E_2^2E_3,$$
$$P(2\omega_3+\omega_1) = 3\epsilon_0\chi^{(3)}E_3^2E_1, \qquad P(2\omega_3+\omega_2) = 3\epsilon_0\chi^{(3)}E_3^2E_2,$$
$$P(2\omega_1-\omega_2) = 3\epsilon_0\chi^{(3)}E_1^2E_2^*, \qquad P(2\omega_1-\omega_3) = 3\epsilon_0\chi^{(3)}E_1^2E_3^*,$$
$$P(2\omega_2-\omega_1) = 3\epsilon_0\chi^{(3)}E_2^2E_1^*, \qquad P(2\omega_2-\omega_3) = 3\epsilon_0\chi^{(3)}E_2^2E_3^*,$$
$$P(2\omega_3-\omega_1) = 3\epsilon_0\chi^{(3)}E_3^2E_1^*, \qquad P(2\omega_3-\omega_2) = 3\epsilon_0\chi^{(3)}E_3^2E_2^*$$

Distinct permutation





Parametric versus Nonparametric Processes

- ***Parametric***

  - Parametric : a process in which the initial and final quantum-mechanical states of the system are identical
  - In a parametric process, population can be removed from the ground state only for those brief intervals of time when it resides in a virtual level
  - By uncertainty principle, population can reside in a virtual level for a time interval

$$\sim \hbar / \delta E$$

◆ δE : energy difference between the virtual level and the nearest real level

- ***Nonparametric***

  - Processes that do involve the transfer of population from one real level to another

Parametric versus Nonparametric Processes

- ***Parametric vs Nonparametric***

  - Parametric : always be described by a real susceptibility
  - Nonparametric : described by a complex susceptibility

  - Parametric : Photon energy is always conserved.
  - Nonparametric : Photon energy need not be conserved

    ◆ Because energy can be transferred to or from the material medium

- ***Example of parametric vs nonparametric***

  - Parametric : real part of the refractive index
  - Nonparametric : imaginary part of the refractive index describes the absorption of radiation

    ◆ It results from the transfer of population from the atomic ground state to an excited state

$$E(r) \sim e^{ikr} = e^{i\left(\frac{n_R}{c}\right)\omega r} e^{i(i)\left(\frac{n_I}{c}\right)\omega r} = E_R e^{-\left(\frac{n_I}{c}\right)\omega r}$$

Saturable Absorption

- ***Saturable Absorption***

  - Many material systems : absorption coefficient decreases when the laser intensity is high

$$\alpha = \frac{\alpha_0}{1 + I/I_s}$$

  - α_0 : low-intensity absorption coefficient
  - I_s : saturation intensity

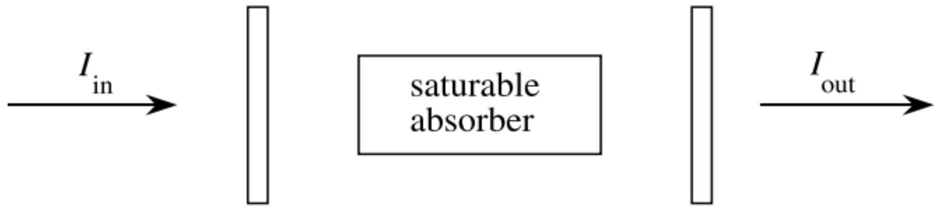
- ***Absorption Coefficient***

$$\alpha = -\left(\frac{1}{I}\right)\left(\frac{dI}{dz}\right), \qquad I(z) = I(0)\exp(-\alpha z)$$

Saturable Absorption

- ***Optical Bistability***

  - Bistable optical device : a saturable absorber inside a Fabry-Perot resonator

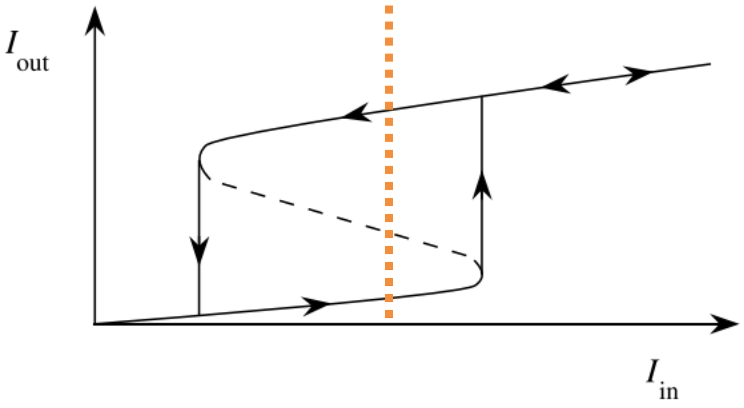


$$\alpha = \frac{\alpha_0}{1 + I/I_s}$$

Input intensity ↑ → field in the cavity ↑ → absorption ↓ → field intensity ↑

  - Subsequently, if input intensity is lowered, the field intensity tends to remain large

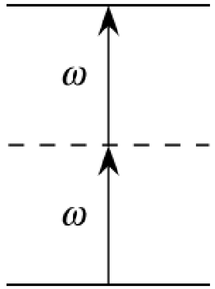
◆ Absorption of the material system has already been reduced (saturated)



Over some range of input intensities more than one output intensity is possible

Two Photon Absorption

- ***Two photon absorption***



- An atom makes a transition from its ground state to an excited state by the simultaneous absorption of two laser photons

- Absorption cross section σ : ***the total area of incident beam is scattered by the target***

$$\sigma = \sigma^{(2)} I$$

- $\sigma^{(2)}$: coefficient that describes strength of the two-photon-absorption process
  - ◆ In linear optics, σ is a constant

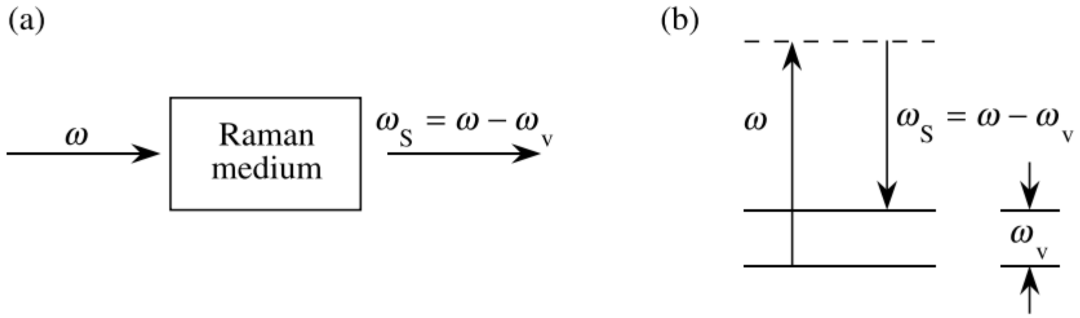
- Atomic transition rate R

$$R = \frac{\sigma I}{\hbar\omega} = \frac{\sigma^{(2)} I^2}{\hbar\omega}$$

- Application : spectroscopic tool for determining the positions of energy levels that are not connected to the atomic ground state by a one-photon transition

Stimulated Raman Scattering

- ***Stimulated Raman Scattering***



- A photon (ω) is annihilated and a photon at the Stokes-shifted frequency $\omega_s = \omega - \omega_v$ is created
- Leaving the molecule (or atom) in an excited state with energy $\hbar\omega_v$ ***Vibrational energy***
- The efficiency of ***stimulated Raman scattering*** can be quite large $\sim 10\%$ or more of the power
- The efficiency of ***normal or spontaneous Raman scattering*** is many orders of magnitude lower
- Other stimulated scattering processes also occur. (Brillouin, Rayleigh scattering)

1.3 Formal Definition of the Nonlinear Susceptibility

E-field of the Frequency Components

- ***General case of a material with dispersion and/or absorption***
  - Nonlinear susceptibility : a complex quantity
  - Assuming the E-field vector as the discrete sum of a number of frequency components

$$\tilde{\boldsymbol{E}}(\boldsymbol{r},t) = \sum_n{}' \tilde{\boldsymbol{E}}_n(\boldsymbol{r},t)$$

Summation over positive frequency

$$\tilde{\boldsymbol{E}}_n(\boldsymbol{r},t) = \boldsymbol{E}_n(\boldsymbol{r})e^{-i\omega_n t} + c.c.$$

  - Assuming that to define the spatially slowly varying field amplitude $\boldsymbol{A}_n$

$$\boldsymbol{E}_n(\boldsymbol{r}) = \boldsymbol{A}_n \boldsymbol{e}^{i\boldsymbol{k}_n\cdot\boldsymbol{r}}$$

$$\mathbf{E}_n = \mathbf{E}(\omega_n) \quad \text{and} \quad \mathbf{A}_n = \mathbf{A}(\omega_n),$$

$$\tilde{\boldsymbol{E}}(\boldsymbol{r},t) = \sum_n{}' \boldsymbol{A}_n \boldsymbol{e}^{i(\boldsymbol{k}_n\cdot\boldsymbol{r}-\omega_n t)} + c.c.$$

$$\mathbf{E}(-\omega_n) = \mathbf{E}(\omega_n)^* \quad \text{and} \quad \mathbf{A}(-\omega_n) = \mathbf{A}(\omega_n)^*$$

  - Rewrite the total field

$$\tilde{\boldsymbol{E}}(\boldsymbol{r},t) = \sum_n \boldsymbol{E}(\omega_n)e^{-i\omega_n t} = \sum_n \boldsymbol{A}(\omega_n)\boldsymbol{e}^{i(\boldsymbol{k}_n\cdot\boldsymbol{r}-\omega_n t)}$$

E-field of the Frequency Components (cont.)

- ***General case of a material with dispersion and/or absorption***

  - Definition of field amplitude

$$\tilde{\boldsymbol{E}}(\boldsymbol{r},t) = \sum_n \boldsymbol{E}(\omega_n)e^{-i\omega_n t} = \left[\boldsymbol{E}(\omega_1)e^{-i\omega_1 t} + \boldsymbol{E}(-\omega_1)e^{i\omega_1 t}\right] + \left(\left[\boldsymbol{E}(\omega_2)e^{-i\omega_2 t} + \boldsymbol{E}(-\omega_2)e^{i\omega_2 t}\right]\right) + \cdots$$

$$\boxed{\tilde{\boldsymbol{E}}(\boldsymbol{r},t) = \mathcal{E}\cos(\mathbf{k}\cdot\mathbf{r} - \omega t)} \qquad \mathbf{E}(\omega) = \frac{1}{2}\mathcal{E}e^{i\mathbf{k}\cdot\mathbf{r}}, \qquad \mathbf{E}(-\omega) = \frac{1}{2}\mathcal{E}e^{-i\mathbf{k}\cdot\mathbf{r}}$$

  - Or alternatively, by the slowly varying amplitude

$$\boldsymbol{A}(\omega) = \frac{1}{2}\boldsymbol{\mathcal{E}}, \qquad \boldsymbol{A}(-\omega) = \frac{1}{2}\mathcal{E}$$

  - The nonlinear polarization

$$\tilde{\boldsymbol{P}}(\boldsymbol{r},t) = \sum_n \boldsymbol{P}(\omega_n)e^{-i\omega_n t}$$

Second-order Nonlinear Polarization

- ***Define the components of the second-order susceptibility tensor (constant)***

$$\chi_{ijk}^{(2)}(\omega_n + \omega_m, \omega_n, \omega_m)$$

- Nonlinear polarization is proportional to second-order susceptibility tensor

$$P_i(\omega_n + \omega_m) = \epsilon_0 \sum_{jk} \sum_{(nm)} \chi_{ijk}^{(2)}(\omega_n + \omega_m, \omega_n, \omega_m) E_j(\omega_n) E_k(\omega_m)$$

◆ ijk : Cartesian components of the fields

◆ (nm): Summation over n, m

◆ $E_j(\omega_n)E_k(\omega_m) \sim e^{-i(\omega_n+\omega_m)t}$: Nonlinear polarization oscillates at $(\omega_n + \omega_m)$

◆ $\chi_{ijk}^{(2)}(\omega_n + \omega_m, \omega_n, \omega_m)$: sometimes written as $\chi_{ijk}^{(2)}(\omega_n + \omega_m; \omega_n, \omega_m)$ because $\omega_3 = \omega_1 + \omega_3$

- Let's examine two simple examples

Sum Frequency Generation

- ***SFG :*** $\omega_3 = \omega_1 + \omega_2$

$$P_i(\omega_3) = \epsilon_0 \sum_{jk} \left[\chi^{(2)}_{ijk}(\omega_3; \omega_1, \omega_2) E_j(\omega_1) E_k(\omega_2) + \underline{\chi^{(2)}_{ijk}(\omega_3; \omega_2, \omega_1) E_j(\omega_2) E_k(\omega_1)} \right]$$

$$\chi^{(2)}_{ikj}(\omega_3; \omega_1, \omega_2) E_j(\omega_1) E_k(\omega_2)$$

  - j, k : dummy indices, they can be interchanged
  - Assuming that the nonlinear susceptibility possesses ***intrinsic permutation symmetry***

$$\chi^{(2)}_{ijk}(\omega_3; \omega_1, \omega_2) = \chi^{(2)}_{ikj}(\omega_3; \omega_2, \omega_1)$$

$$P_i(\omega_3) = 2\epsilon_0 \sum_{jk} \chi^{(2)}_{ijk}(\omega_3; \omega_1, \omega_2) E_j(\omega_1) E_k(\omega_2)$$

  - For the special case, both input fields are polarized in the x direction

$$P_i(\omega_3) = 2\epsilon_0 \chi^{(2)}_{ixx}(\omega_3; \omega_1, \omega_2) E_x(\omega_1) E_x(\omega_2)$$

Sum Harmonic Generation

- ***SHG : input frequency as*** ω_3, $\omega_3 = 2\omega_1$

$$P_i(\omega_3) = \epsilon_0 \sum_{jk} \chi^{(2)}_{ijk}(\omega_3; \omega_1, \omega_1) E_j(\omega_1) E_k(\omega_1) \quad \textbf{SHG}$$

  - Assuming both input fields are polarized in the x direction

$$P_i(\omega_3) = \epsilon_0 \chi^{(2)}_{ixx}(\omega_3; \omega_1, \omega_1) E_x(\omega_1)^2$$

- ***About a factor of 2***

$$P_i(\omega_3) = 2\epsilon_0 \sum_{jk} \chi^{(2)}_{ijk}(\omega_3; \omega_1, \omega_2) E_j(\omega_1) E_k(\omega_2) \quad \textbf{SFG}$$

  - As ω_2 goes ω_1, $\chi^{(2)}_{ijk}(\omega_3; \omega_1, \omega_1)$ must approach $\chi^{(2)}_{ijk}(\omega_3; \omega_1, \omega_2)$ in SFG
  - Why doesn't the factor of 2 appear at first in the SHG expression?
    Because our susceptibility convention lists each input frequency in an ordered permutation

◆ Someone thought : "polarization produced by two distinct fields is larger than that produced by single field"

NO

  - Define the degeneracy factor D that is equal to the number of distinct permutations of the applied field

Degeneracy Factor and Third-order Susceptibility

- ***Considering with degeneracy factor D***

$$P_i(\omega_n + \omega_m) = \epsilon_0 D \sum_{jk} \chi^{(2)}_{ijk}(\omega_n + \omega_m, \omega_n, \omega_m) E_j(\omega_n) E_k(\omega_m)$$

- ***Third-order susceptibility***

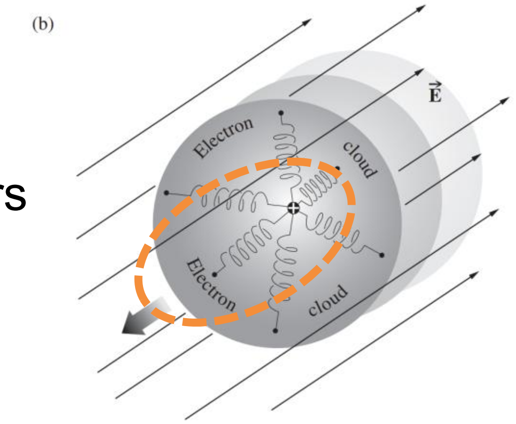
$$P_i(\omega_o + \omega_n + \omega_m) = \epsilon_0 \sum_{jk} \chi^{(3)}_{ijkl}(\omega_o + \omega_n + \omega_m, \omega_o, \omega_n, \omega_m) E_j(\omega_o) E_k(\omega_n) E_l(\omega_m)$$

  - Considering with degeneracy factor that represents the number of distinct permutations of the frequencies

$$P_i(\omega_o + \omega_n + \omega_m) = \epsilon_0 D \sum_{jk} \chi^{(3)}_{ijkl}(\omega_o + \omega_n + \omega_m, \omega_o, \omega_n, \omega_m) E_j(\omega_o) E_k(\omega_n) E_l(\omega_m)$$

1.4 Nonlinear Susceptibility of a Classical Anharmonic Oscillator

E-field of the Frequency Components



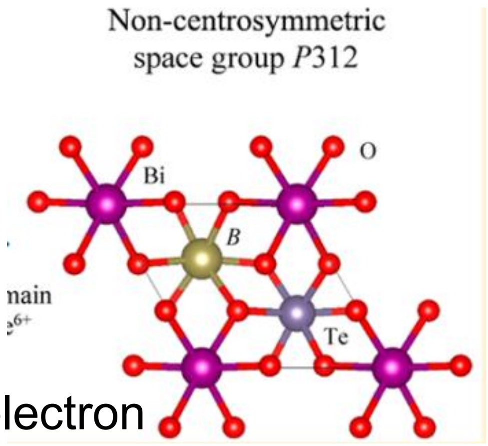
- ***Lorentz model of the atom***
  - The Lorentz model treats the atom as a harmonic oscillator
  - It provides a good description of the linear optical properties of atomic vapors

- ***Nonlinearity of Lorentz model of the atom***
  - Extending the restoring force
  - The details of the analysis differ depending upon “inversion symmetry of the medium”

- ***Defect of Lorentz model***
  - A single resonance frequency ω_0 to each atom : only one resonance frequency
  - In quantum-mechanical theory, it allows each atom to possess many energy eigenvalues and hence than one resonance frequency

Noncentrosymmetric Media

F. Ding et al., Inorg. Chem. 57, 7950 (2018).

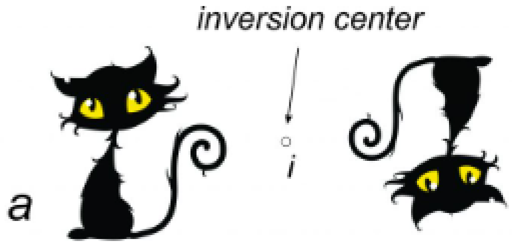


- ***For noncentrosymmetric medium (electron position : $\tilde{x}$)***

$$\ddot{\tilde{x}} + 2\gamma\dot{\tilde{x}} + \omega_0^2\tilde{x} + \boxed{a\tilde{x}^2} = -e\tilde{E}(t)/m$$

- $\tilde{E}(t)$: applied E-field, $-e$: the charge of the electron and damping force : $-2m\gamma\dot{\tilde{x}}$
- Restoring force : assuming that it is a nonlinear function of the displacement of the electron

$$\tilde{F}_{restoring} = -m\omega_0^2\tilde{x} - ma\tilde{x}^2$$



- a : parameter about the strength of the nonlinearity
- Potential energy

Anharmonic correction

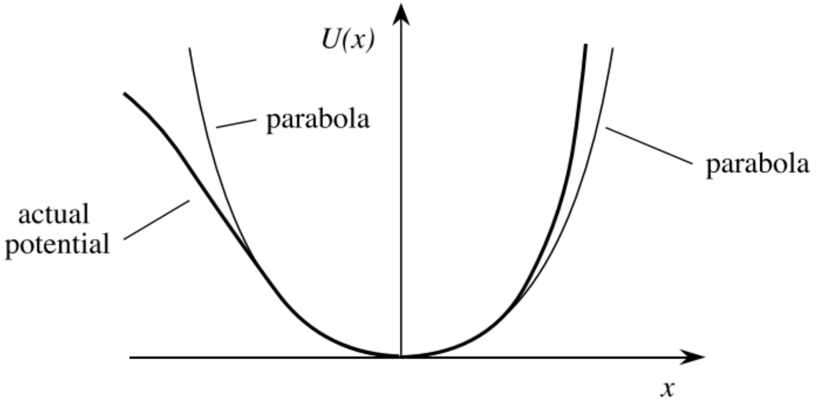
$$U(\tilde{x}) = -\int \tilde{F}_{restoring}d\tilde{x} = \frac{1}{2}m\omega_0^2\tilde{x}^2 + \boxed{\frac{1}{3}ma\tilde{x}^3}$$

- Not perfectly parabolic
- Even and odd powers of $\tilde{x}$
- Scalar-field approximation : cannot treat the tensor of the nonlinear susceptibility without assumption about symmetry

https://opengeology.org/Mineralogy/10-crystal-morphology-and-symmetry/

Perturbation Expansion Approach

- ***Potential energy for a noncentrosymmetric medium***



$$\ddot{\tilde{x}} + 2\gamma\dot{\tilde{x}} + \omega_0^2\tilde{x} + a\tilde{x}^2 = -e\tilde{E}(t)/m$$

- Assuming the applied optical field $E_1 = E(\omega_1), E_2 = E(\omega_2)$

$$\tilde{E}(t) = E_1 e^{-i\omega_1 t} + E_2 e^{-i\omega_2 t} + c.c.$$

- Assuming that the applied is sufficiently weak : $\omega_0^2\tilde{x} \gg a\tilde{x}^2$
  - Can be solved by means of a ***perturbation expansion***

$$\tilde{E}(t) \to \lambda\tilde{E}(t), 0 < \lambda \leq 1$$

  - Input $\lambda = 1$ when finishing calculation

$$\ddot{\tilde{x}} + 2\gamma\dot{\tilde{x}} + \omega_0^2\tilde{x} + a\tilde{x}^2 = -e\lambda\tilde{E}(t)/m$$

- A solution is the form of a power-series expansion in the λ

$$\tilde{x} = \lambda\tilde{x}^{(1)} + \lambda^2\tilde{x}^{(2)} + \lambda^3\tilde{x}^{(3)} + \cdots$$

Perturbation Expansion Approach

$$\boxed{\begin{gathered}\ddot{\tilde{x}} + 2\gamma\dot{\tilde{x}} + \omega_0^2\tilde{x} + a\tilde{x}^2 = -e\lambda\tilde{E}(t)/m \\ \tilde{x} = \lambda\tilde{x}^{(1)} + \lambda^2\tilde{x}^{(2)} + \lambda^3\tilde{x}^{(3)} + \cdots\end{gathered}}$$

$$\tilde{x}^2 = \lambda^2\left[\tilde{x}^{(1)}\right]^2 + 2\lambda^3\tilde{x}^{(1)}\tilde{x}^{(2)} + \cdots$$

λ $$\ddot{\tilde{x}}^{(1)} + 2\gamma\dot{\tilde{x}}^{(1)} + \omega_0^2\tilde{x}^{(1)} = -e\tilde{E}(t)/m$$ ***(linear) Lorentz model***

λ^2 $$\ddot{\tilde{x}}^{(2)} + 2\gamma\dot{\tilde{x}}^{(2)} + \omega_0^2\tilde{x}^{(2)} + a\left[\tilde{x}^{(1)}\right]^2 = 0$$

λ^3 $$\ddot{\tilde{x}}^{(3)} + 2\gamma\dot{\tilde{x}}^{(3)} + \omega_0^2\tilde{x}^{(3)} + 2\tilde{x}^{(1)}\tilde{x}^{(2)} = 0$$

- Steady state solution in (linear) Lorentz model

$$\tilde{x}^{(1)}(t) = x^{(1)}(\omega_1)e^{-i\omega_1 t} + x^{(1)}(\omega_2)e^{-i\omega_2 t} + c.c.$$

$$x^{(1)}(\omega_j) = -\frac{e}{m}\frac{E_j}{D(\omega_j)}$$

$$D(\omega_j) = \omega_0^2 - \omega_j^2 - 2i\omega_j\gamma$$

Perturbation Expansion Approach

λ^2

$$\ddot{\tilde{x}}^{(2)} + 2\gamma\dot{\tilde{x}}^{(2)} + \omega_0^2\tilde{x}^{(2)} + a\left[\tilde{x}^{(1)}\right]^2 = 0$$

- The square of $\tilde{x}^{(1)}$ contains several frequencies

$$\tilde{x}^{(1)}(t) = x^{(1)}(\omega_1)e^{-i\omega_1 t} + x^{(1)}(\omega_2)e^{-i\omega_2 t} + c.c.$$

$$\pm 2\omega_1, \pm 2\omega_2, \pm(\omega_1 + \omega_2), \pm(\omega_1 - \omega_2)\ and\ 0$$

- Choose the response at frequency $2\omega_1$ for instance,

$$\ddot{\tilde{x}}^{(2)} + 2\gamma\dot{\tilde{x}}^{(2)} + \omega_0^2\tilde{x}^{(2)} = -a\left(\frac{eE_1}{m}\right)^2 \frac{e^{-2i\omega_1 t}}{D^2(\omega_1)}$$

- Steady state solution

$$\tilde{x}^{(2)}(t) = x^{(2)}(2\omega_1)e^{-2i\omega_1 t}$$

$$x^{(2)}(2\omega_1) = \left[-a\left(\frac{eE_1}{m}\right)^2 \frac{1}{D^2(\omega_1)}\right]\frac{1}{D(2\omega_1)} = \frac{-a(e/m)^2E_1^2}{D(2\omega_1)D^2(\omega_1)}$$

Another examples,

$$x^{(2)}(2\omega_2) = \frac{-a(e/m)^2E_2^2}{D(2\omega_2)D^2(\omega_2)},$$

$$x^{(2)}(\omega_1+\omega_2) = \frac{-2a(e/m)^2E_1E_2}{D(\omega_1+\omega_2)D(\omega_1)D(\omega_2)},$$

$$x^{(2)}(\omega_1-\omega_2) = \frac{-2a(e/m)^2E_1E_2^*}{D(\omega_1-\omega_2)D(\omega_1)D(-\omega_2)},$$

$$x^{(2)}(0) = \frac{-2a(e/m)^2E_1E_1^*}{D(0)D(\omega_1)D(-\omega_1)} + \frac{-2a(e/m)^2E_2E_2^*}{D(0)D(\omega_2)D(-\omega_2)}.$$

$\omega_1 - \omega_1$ and $\omega_2 - \omega_2$

Linear Susceptibility

- ***Linear susceptibility ($\chi^{(1)}$)***

Number density of atoms

$$P^{(1)}(\omega_j) = \epsilon_0 \chi^{(1)}(\omega_j) E(\omega_j) = -Nex^{(1)}(\omega_j)$$

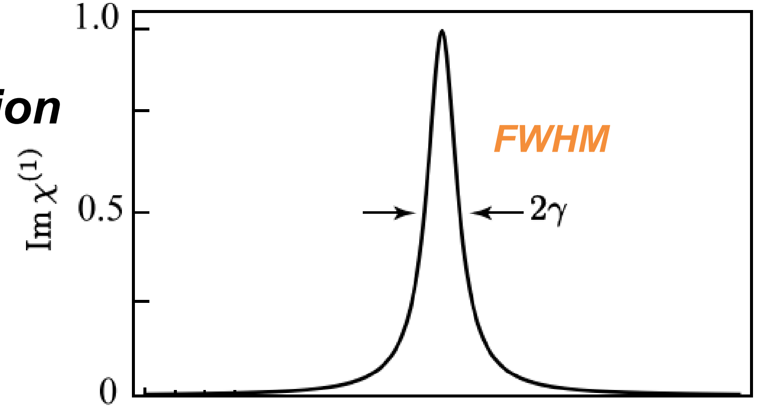
$$\chi^{(1)}(\omega_j) = -\frac{Ne}{\epsilon_0}\frac{1}{E_j}x^{(1)}(\omega_j) = \frac{Ne^2}{\epsilon_0 m}\frac{1}{D(\omega_j)}$$

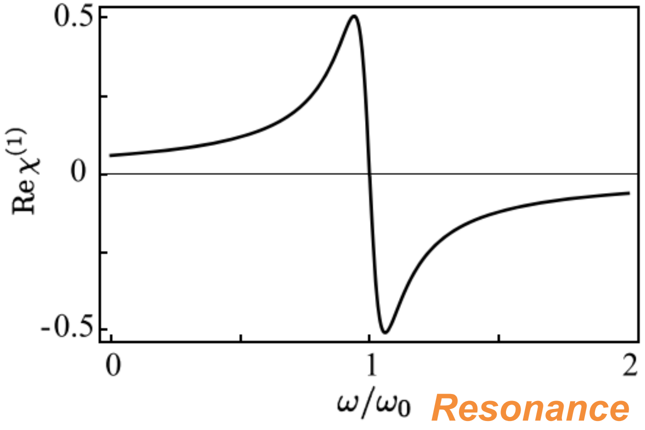
  - Close to resonance $\omega_j \approx \omega_0$

$$D(\omega_j) = \omega_0^2 - \omega_j^2 - 2i\omega_j\gamma = (\omega_0 + \omega_j)(\omega_0 - \omega_j) - 2i\omega_j\gamma \approx 2\omega_0(\omega_j - \omega_0 - i\gamma)$$

$$\chi^{(1)}(\omega_j) = \frac{Ne^2}{2\epsilon_0 m\omega_0}\frac{1}{(\omega_j - \omega_0 - i\gamma)} = \frac{Ne^2}{2\epsilon_0 m\omega_0}\frac{(\omega_j - \omega_0) + i\gamma}{(\omega_j - \omega_0)^2 + \gamma^2}$$

Atomic absorption profile





Nonlinear Susceptibility

- ***Nonlinear susceptibility ($\chi^{(2)}$)***

Number density of atoms

$$P^{(2)}(2\omega_1) = \epsilon_0 \chi^{(2)}(2\omega_1; \omega_1, \omega_1) E(\omega_1)^2 = -Nex^{(2)}(2\omega_1)$$

$$\chi^{(2)}(2\omega_1; \omega_1, \omega_1) = -\frac{Ne}{\epsilon_0} \frac{1}{E(\omega_1)^2} x^{(2)}(2\omega_1) = \frac{Ne^3 a}{\epsilon_0 m^2} \frac{1}{D(2\omega_1) D^2(\omega_1)}$$

- In terms of the product of linear susceptibilities

$$\chi^{(2)}(2\omega_1; \omega_1, \omega_1) = \frac{\epsilon_0 ma}{Ne^3} \chi^{(1)}(2\omega_1) \left[\chi^{(1)}(\omega_1)\right]^2$$

$$\boxed{\chi^{(1)}(\omega_1) = \frac{Ne^2}{\epsilon_0 m} \frac{1}{D(\omega_1)}}$$

  - ◆ Second-order susceptibility as a function of three frequencies

- For SFG case, one (ω_1) of the fields goes ω_2 and DFG case, Optical rectification (ω_1) case are

$$\chi^{(2)}(\omega_1 + \omega_2; \omega_1, \omega_2) = \frac{\epsilon_0 ma}{Ne^3} \chi^{(1)}(\omega_1 + \omega_2) \chi^{(1)}(\omega_1) \chi^{(1)}(\omega_2)$$

$$\chi^{(2)}(\omega_1 - \omega_2; \omega_1, -\omega_2) = \frac{\epsilon_0 ma}{Ne^3} \chi^{(1)}(\omega_1 - \omega_2) \chi^{(1)}(\omega_1) \chi^{(1)}(-\omega_2)$$

$$\chi^{(2)}(0; \omega_1, -\omega_1) = \frac{\epsilon_0 ma}{Ne^3} \chi^{(1)}(0) \chi^{(1)}(\omega_1) \chi^{(1)}(-\omega_1)$$

- If you want to know $\chi^{(n)}$ susceptibility, you should expand λ^n

Miller's Rule

- ***Empirical rule due to Miller***

$$\frac{\chi^{(2)}(\omega_1+\omega_2;\omega_1,\omega_2)}{\chi^{(1)}(\omega_1+\omega_2)\chi^{(1)}(\omega_1)\chi^{(1)}(\omega_2)}$$

  - Nearly constant for all noncentrosymmetric crystals

$$\frac{\frac{\epsilon_0 ma}{Ne^3}\chi^{(1)}(\omega_1+\omega_2)\chi^{(1)}(\omega_1)\chi^{(1)}(\omega_2)}{\chi^{(1)}(\omega_1+\omega_2)\chi^{(1)}(\omega_1)\chi^{(1)}(\omega_2)} = \frac{\epsilon_0 ma}{Ne^3}$$

Nearly constant

    - Atomic number density N : $\sim 10^{22}\ \mathrm{cm}^{-3}$ for all condensed matter and m, e are constant

  - The size of the nonlinear coefficient a by the linear and nonlinear contributions to the restoring force
    - Assuming that $\tilde{x}\ \approx$ size of the atom (separation between atoms; lattice constant d)
    - This reasoning leads to the order-of-magnitude estimate $m\omega_0^2 d = mad^2$

By reasons of nonsymmetry, $a \neq 0$ $\qquad a = \omega_0^2/d \qquad$ ***Roughly the same for all materials***

Nonlinear Coefficient

- ***The estimate of nonlinear coefficient***

$$D(\omega_j) = \omega_0^2 - \omega_j^2 - 2i\omega_j\gamma \approx \omega_0^2$$

  - To estimate of the size of the second-order susceptibility under ***highly nonresonant conditions***

$$N = 1/d^3$$

$$\chi^{(2)}(\omega_1 + \omega_2; \omega_1, \omega_2) = \frac{Ne^3 a}{\epsilon_0 m^2} \frac{1}{D(\omega_1 + \omega_2) D(\omega_1) D(\omega_2)} \approx \frac{Ne^3 a}{\epsilon_0 m^2 \omega_0^6} = \frac{e^3}{\epsilon_0 m^2 \omega_0^4 d^4}$$

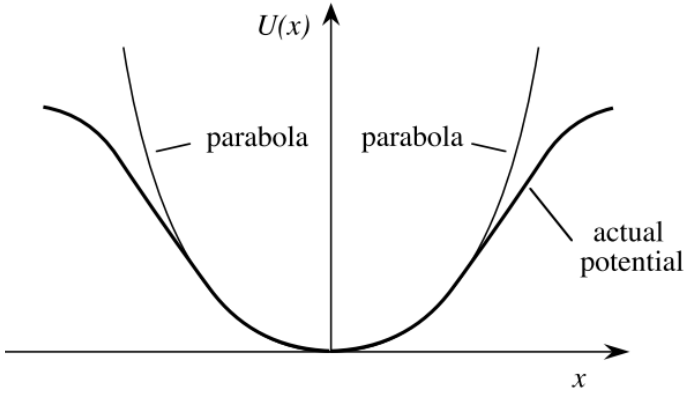
Using the typical values $\omega_0 = 1 \times 10^{16}$ rad/s, $d = 3$ Å, $e = 1.6 \times 10^{-19}$ C, and $m = 9.1 \times 10^{-31}$ kg, we find that

$$\chi^{(2)} \simeq 6.9 \times 10^{-12} \text{ m/V}, \tag{1.4.32}$$

Centrosymmetric Media

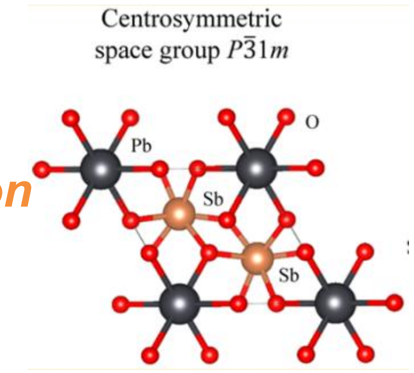
F. Ding et al., Inorg. Chem. 57, 7950 (2018).

▪ ***Electronic restoring force for centrosymmetric medium***

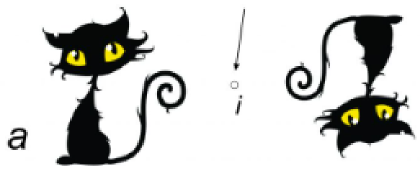


$$\tilde{F}_{restoring} = -m\omega_0^2\tilde{x} - mb\tilde{x}^3$$ lowest-order correction

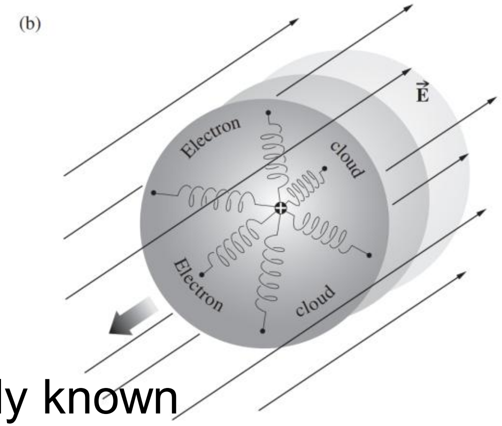
$$U(\tilde{x}) = -\int \tilde{F}_{restoring}\, d\tilde{x} = \frac{1}{2}m\omega_0^2\tilde{x}^2 - \frac{1}{4}mb\tilde{x}^4$$



- b : the strength of the nonlinearity (usually positive value)



- Symmetry under the operation : $\tilde{x} \rightarrow -\tilde{x}$
  - ◆ A center of inversion symmetry
- Assuming that the electronic displacement $\tilde{x}$ never becomes so large
- Nonlinear term contributes to third-order polarization as a $\chi^{(3)}$ susceptibility
- Cannot be specified unless the internal symmetries of the medium are completely known
  - ◆ Assuming that a material is ***isotropic***
  - ◆ For examples, glasses and liquids



https://opengeology.org/Mineralogy/10-crystal-morphology-and-symmetry/

Equation of Motion for Isotropic Material

- ***The equation of motion for the isotropic material***

$$\tilde{\boldsymbol{F}}_{restoring} = -m\omega_0^2\tilde{\boldsymbol{r}} - mb(\tilde{\boldsymbol{r}}\cdot\tilde{\boldsymbol{r}})\tilde{\boldsymbol{r}}$$

$$\ddot{\tilde{\boldsymbol{r}}} + 2\gamma\dot{\tilde{\boldsymbol{r}}} + \omega_0^2\tilde{\boldsymbol{r}} - b(\tilde{\boldsymbol{r}}\cdot\tilde{\boldsymbol{r}})\tilde{\boldsymbol{r}} = -e\tilde{\boldsymbol{E}}(t)/m$$

  - Assuming the input field has three distinct frequency components (for three-order interaction)

$$\tilde{\boldsymbol{E}}(t) = \sum_n \boldsymbol{E}(\omega_n)e^{-i\omega_n t}$$

  - If anharmonics term is very weak, we can also use perturbation

$$\tilde{\boldsymbol{E}}(t) \to \lambda\tilde{\boldsymbol{E}}(t), 0 < \lambda \leq 1$$

$$\tilde{\boldsymbol{r}} = \lambda\tilde{\boldsymbol{r}}^{(1)} + \lambda^2\tilde{\boldsymbol{r}}^{(2)} + \lambda^3\tilde{\boldsymbol{r}}^{(3)} + \cdots$$

  - As in the previous case about λ^n,

$$\ddot{\tilde{\boldsymbol{r}}}^{(1)} + 2\gamma\dot{\tilde{\boldsymbol{r}}}^{(1)} + \omega_0^2\tilde{\boldsymbol{r}}^{(1)} = -e\tilde{\boldsymbol{E}}(t)/m$$

$$\ddot{\tilde{\boldsymbol{r}}}^{(2)} + 2\gamma\dot{\tilde{\boldsymbol{r}}}^{(2)} + \omega_0^2\tilde{\boldsymbol{r}}^{(2)} = 0$$

$$\ddot{\tilde{\boldsymbol{r}}}^{(3)} + 2\gamma\dot{\tilde{\boldsymbol{r}}}^{(3)} + \omega_0^2\tilde{\boldsymbol{r}}^{(3)} - b\left(\tilde{\boldsymbol{r}}^{(1)}\cdot\tilde{\boldsymbol{r}}^{(1)}\right)\tilde{\boldsymbol{r}}^{(1)} = 0$$

Linear Susceptibility

- ***Steady-state solution***

$$\tilde{\boldsymbol{r}}^{(1)}(t) = \sum_n \boldsymbol{r}^{(1)}(\omega_n) e^{-i\omega_n t}, \qquad \boldsymbol{r}^{(1)}(\omega_n) = -\frac{e}{m}\frac{\boldsymbol{E}(\omega_n)}{D(\omega_n)}$$

- The Cartesian components of the polarization

$$\boldsymbol{P}^{(1)}(\omega_n) = -Ne\boldsymbol{r}^{(1)}(\omega_n)$$

$$P_i^{(1)}(\omega_n) = \epsilon_0 \sum_j \chi_{ij}^{(1)}(\omega_n) E_j(\omega_n)$$

- Principal axes in linear susceptibility

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

$$\chi^{(1)}(\omega_n) = \frac{Ne^2}{m}\frac{1}{D(\omega_n)}$$

- The second-order response is not driven, $\tilde{\boldsymbol{r}}^{(2)} = 0$

Third-order Response

- ***Third-order response***

$$\ddot{\tilde{\boldsymbol{r}}}^{(3)} + 2\gamma\dot{\tilde{\boldsymbol{r}}}^{(3)} + \omega_0^2\tilde{\boldsymbol{r}}^{(3)} - b\left(\tilde{\boldsymbol{r}}^{(1)} \cdot \tilde{\boldsymbol{r}}^{(1)}\right)\tilde{\boldsymbol{r}}^{(1)} = 0$$

$$\left(\tilde{\boldsymbol{r}}^{(1)} \cdot \tilde{\boldsymbol{r}}^{(1)}\right)\tilde{\boldsymbol{r}}^{(1)} = -\frac{e^3}{m^3}\frac{[\boldsymbol{E}(\omega_m) \cdot \boldsymbol{E}(\omega_n)]\boldsymbol{E}\left(\omega_p\right)}{D(\omega_m)D(\omega_n)D\left(\omega_p\right)}e^{-i(\omega_m+\omega_n+\omega_p)t}$$

- Let these frequencies be $\omega_q \equiv \omega_m + \omega_n + \omega_p$

$$\tilde{\boldsymbol{r}}^{(3)}(t) = \sum_q \boldsymbol{r}^{(3)}\left(\omega_q\right)e^{-i\omega_q t}$$

$$\left(-\omega_q^2 - iw_q 2\gamma + \omega_0^2\right)\tilde{\boldsymbol{r}}^{(3)}\left(\omega_q\right) = -\sum_{(mnp)}\frac{be^3}{m^3}\frac{[\boldsymbol{E}(\omega_m) \cdot \boldsymbol{E}(\omega_n)]\boldsymbol{E}\left(\omega_p\right)}{D(\omega_m)D(\omega_n)D\left(\omega_p\right)}$$

- $D\left(\omega_q\right) = \omega_q^2 - iw_q 2\gamma + \omega_0^2$

$$\tilde{\boldsymbol{r}}^{(3)}\left(\omega_q\right) = -\sum_{(mnp)}\frac{be^3}{m^3}\frac{[\boldsymbol{E}(\omega_m) \cdot \boldsymbol{E}(\omega_n)]\boldsymbol{E}\left(\omega_p\right)}{D\left(\omega_q\right)D(\omega_m)D(\omega_n)D\left(\omega_p\right)}$$

Third-order Response (cont.)

- ***Third-order nonlinear susceptibility***

$$\boldsymbol{P}_i^{(3)}(\omega_q) = -Ne\boldsymbol{r}^{(3)}(\omega_q)$$

$$P_i^{(3)}(\omega_q) = \epsilon_0 \sum_{jkl} \sum_{(mnp)} \chi_{ijkl}^{(3)}(\omega_q;\omega_m,\omega_n,\omega_p) \boxed{E_j(\omega_m)E_k(\omega_n)E_l(\omega_p)}$$

- Linear susceptibility has only principal axes and isotropic properties

$$\chi_{ijkl}^{(3)}(\omega_q;\omega_m,\omega_n,\omega_p) = \frac{Nbe^4}{\epsilon_0 m^3} \frac{\delta_{jk}\delta_{il}}{D(\omega_q)D(\omega_m)D(\omega_n)D(\omega_p)}$$

$$\boxed{\chi^{(1)}(\omega_n) = \frac{Ne^2}{m}\frac{1}{D(\omega_n)}}$$

- ***Intrinsic permutation symmetry*** : Six possible permutations
  - So, we define one-six of the sum of the six expression

$$\chi_{ijkl}^{(3)}(\omega_q;\omega_m,\omega_n,\omega_p) = \frac{Nbe^4}{6\epsilon_0 m^3} \frac{2(\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{jk}\delta_{il})}{D(\omega_q)D(\omega_m)D(\omega_n)D(\omega_p)}$$

$$\chi_{ijkl}^{(3)}(\omega_q;\omega_m,\omega_n,\omega_p) = \frac{bm\epsilon_0^3}{3N^3e^4}\left[\chi^{(1)}(\omega_q)\chi^{(1)}(\omega_m)\chi^{(1)}(\omega_n)\chi^{(1)}(\omega_n)\right]\left[\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{jk}\delta_{il}\right]$$

Estimate Nonlinear Coefficient

- ***Estimate nonlinear coefficient b***
  - The linear and nonlinear contributions to the restoring force will become comparable in magnitude
  - Atomic dimension d

$$b = \omega_0^2 / d^2$$

  - For nonresonant excitation, $D(\omega) \approx \omega_0^2$

$$\chi_{ijkl}^{(3)}(\omega_q; \omega_m, \omega_n, \omega_p) = \frac{Nbe^4}{\epsilon_0 m^3} \frac{1}{D(\omega_q) D(\omega_m) D(\omega_n) D(\omega_p)} \approx \frac{Nbe^4}{\epsilon_0 m^3 \omega_0^8} = \frac{e^4}{\epsilon_0 m^3 \omega_0^6 d^5}$$

Taking $d = 3$ Å and $\omega_0 = 7 \times 10^{15}$ rad/sec, we obtain

$$\chi^{(3)} \simeq 344 \text{ pm}^2/\text{V}^2 \tag{1.4.56}$$

1.5 Properties of the Nonlinear Susceptibility

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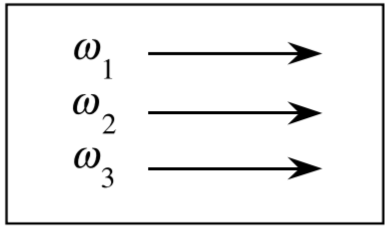
Estimate Nonlinear Coefficient

- ***Symmetry properties***
  - Considering the mutual interaction of three waves of frequencies $\omega_1, \omega_2, \omega_3 = \omega_1 + \omega_2$
  - We should know nonlinear polarization $\boldsymbol{P}(\omega_i)$ for a complete description



$$P_i(\omega_n + \omega_m) = \epsilon_0 \sum_{jk} \sum_{(n,m)} \chi^{(2)}_{ijk}(\omega_n + \omega_m; \omega_n, \omega_m) E_j(\omega_n) E_k(\omega_m)$$

  - Six tensor quantities of positive frequency

$$\chi^{(2)}_{ijk}(\omega_1, \omega_3, -\omega_2), \quad \chi^{(2)}_{ijk}(\omega_1, -\omega_2, \omega_3), \quad \chi^{(2)}_{ijk}(\omega_2, \omega_3, -\omega_1),$$
$$\chi^{(2)}_{ijk}(\omega_2, -\omega_1, \omega_3), \quad \chi^{(2)}_{ijk}(\omega_3, \omega_1, \omega_2), \quad \text{and} \quad \chi^{(2)}_{ijk}(\omega_3, \omega_2, \omega_1)$$

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  - In Cartesian system, $i, j. k \in \{x, y, z\}$ $\quad$ $\mathbf{3^3}$
  - So, If we don't have any information about symmetry, we must know complex components of 324 to describe the interaction
    - ◆ Fortunately, there are a number of restrictions resulting from symmetry

Reality of the Fields

- ***Real value of polarization & susceptibility***

$$\tilde{\boldsymbol{P}}_i(\boldsymbol{r},t) = P_i(\omega_n + \omega_m)e^{-i(\omega_n+\omega_m)t} + P_i(-\omega_n - \omega_m)e^{i(\omega_n+\omega_m)t}$$

$$\boxed{\begin{gathered} P_i(-\omega_n - \omega_m) = P_i(\omega_n + \omega_m)^* \\ E(-\omega) = E(\omega)^* \end{gathered}}$$

  - Purely real : physically measurable

$$\chi^{(2)}_{ijk}(-\omega_n - \omega_m; -\omega_n, -\omega_m) = \chi^{(2)}_{ijk}(\omega_n + \omega_m; \omega_n, \omega_m)^*$$

  - We can directly obtain the negative frequency quantity from positive thing

Intrinsic Permutation Symmetric

- ***Intrinsic permutation symmetric***
  - For dummy indices,

$$P_i(\omega_n+\omega_m)=\epsilon_0\sum_{jk}\sum_{(n,m)}\chi^{(2)}_{ijk}(\omega_n+\omega_m;\omega_n,\omega_m)E_j(\omega_n)E_k(\omega_m)$$

$$j\leftrightarrow k, n\leftrightarrow m$$

$$P_i(\omega_n+\omega_m)=\epsilon_0\sum_{jk}\sum_{(n,m)}\chi^{(2)}_{ikj}(\omega_m+\omega_n;\omega_m,\omega_n)E_k(\omega_m)E_j(\omega_n)$$

$E_x(\omega_1)E_y(\omega_2)$

$E_y(\omega_2)E_x(\omega_1)$ ○

$E_x(\omega_2)E_y(\omega_1)$ ⃠

  - Physically same quantities
    - So, $\chi^{(2)}_{ijk}(\omega_n+\omega_m;\omega_n,\omega_m)$ must be equal to $\chi^{(2)}_{ikj}(\omega_m+\omega_n;\omega_m,\omega_n)$
    - this condition is simply a statement that it cannot matter which is the first field and which is the second field in products

Note that this symmetry condition is introduced purely as a matter of convenience.

Symmetry for Lossless Media

- ***Two additional symmetries of the nonlinear susceptibility tensor***
  - Assuming that our frequencies are far from resonant frequency
  - Susceptibility goes ***real***

$$\chi^{(2)}(\omega_1+\omega_2;\omega_1,\omega_2)=\frac{Ne^3a}{\epsilon_0 m^2}\frac{1}{D(\omega_1+\omega_2)D(\omega_1)D(\omega_2)}\approx\frac{Ne^3a}{\epsilon_0 m^2\omega_0^6}$$

  - Fully permutation symmetry
    - ◆ All of the frequency arguments of the nonlinear susceptibility can be freely interchanged, as long as the corresponding Cartesian indices are interchanged simultaneously

$$\omega_3=\omega_1+\omega_2$$

  - Example of two conditions $\chi^{(2)}_{ijk}(\omega_3=\omega_1+\omega_2)=\chi^{(2)}_{jki}(\omega_1=-\omega_2+\omega_3)$

$$\chi^{(2)}_{ijk}(\omega_3=\omega_1+\omega_2)=\chi^{(2)}_{jki}(-\omega_1=\omega_2-\omega_3)=\chi^{(2)}_{jki}(\omega_1=-\omega_2+\omega_3)^*=\chi^{(2)}_{jki}(\omega_1=-\omega_2+\omega_3)$$

Field Energy Density for a Linear Medium

- ***Full permutation symmetry from EM-field energy***
  - Full permutation symmetry of susceptibility is deduced from EM field energy within a nonlinear medium
  - Energy density according to Poynting's theorem within a linear medium,

$$\tilde{E}_i(t) = \sum_n E_i(\omega_n) e^{-i\omega_n t}$$

$$U = \frac{1}{2}\langle \tilde{\boldsymbol{D}} \cdot \tilde{\boldsymbol{E}} \rangle = \frac{1}{2}\sum_i \langle \tilde{D}_i \tilde{E}_i \rangle$$

  - Displacement vector & dielectric tensor

$$\tilde{D}_i(t) = \epsilon_0 \sum_j \epsilon_{ij} \tilde{E}_j(t) = \epsilon_0 \sum_j \sum_n \epsilon_{ij}(\omega_n) E_j(\omega_n) e^{-i\omega_n t}$$

$$\epsilon_{ij}(\omega_n) = \delta_{ij} + \chi_{ij}^{(1)}(\omega_n)$$

  - Energy density

In vacuum *Polarization of the medium*

$$U = \frac{1}{2}\epsilon_0 \sum_i \sum_n E_i^*(\omega_n) E_i(\omega_n) + \frac{1}{2}\epsilon_0 \sum_{ij} \sum_n \chi_{ij}^{(1)}(\omega_n) E_i^*(\omega_n) E_j(\omega_n)$$

Field Energy Density for a Nonlinear Medium

- ***Full permutation symmetry from EM-field energy***
  - Energy density according to Poynting's theorem within a nonlinear medium,
  - General form is

$$U = \frac{\epsilon_0}{2}\sum_{ij}\sum_{n}\chi_{ij}^{(1)}(\omega_n)E_i^*(\omega_n)E_j(\omega_n) + \frac{\epsilon_0}{3}\sum_{ijk}\sum_{mn}\chi_{ijk}^{(2)'}(-\omega_n-\omega_m;\omega_m,\omega_n)\boxed{E_i^*(\omega_m+\omega_n)E_j(\omega_m)E_k(\omega_n)}$$
$$+\frac{\epsilon_0}{4}\sum_{ijkl}\sum_{mno}\chi_{ijkl}^{(3)'}(-\omega_o-\omega_n-\omega_m;\ \omega_m,\omega_n,\omega_o)\boxed{E_i^*(\omega_m+\omega_n+\omega_o)E_j(\omega_m)E_k(\omega_n)E_l(\omega_o)} + \cdots$$

  - $\chi^{(n)'}$ as coefficients in the power series expansion of U
  - The order of Multiplied E-fields is not immaterial, so, the quantity $\chi^{(n)'}$ is full permutation symmetry
  - The polarization of a medium is given by the expression

$$P_i(\omega_n) = \frac{\partial U}{\partial E_i^*(\omega_n)}$$

Field Energy Density for a Nonlinear Medium

- ***Linear and nonlinear polarization***

$$P_i(\omega_n) = \frac{\partial U}{\partial E_i^*(\omega_n)}$$

$$U = \frac{\epsilon_0}{2}\sum_{ij}\sum_{n}\chi_{ij}^{(1)}(\omega_n)E_i^*(\omega_n)E_j(\omega_n) + \frac{\epsilon_0}{3}\sum_{ijk}\sum_{mn}\chi_{ijk}^{(2)\prime}(-\omega_n-\omega_m;\omega_m,\omega_n)E_i^*(\omega_m+\omega_n)E_j(\omega_m)E_k(\omega_n)$$
$$+\frac{\epsilon_0}{4}\sum_{ijkl}\sum_{mno}\chi_{ijkl}^{(3)\prime}(-\omega_o-\omega_n-\omega_m;\ \omega_m,\omega_n,\omega_o)E_i^*(\omega_m+\omega_n+\omega_o)E_j(\omega_m)E_k(\omega_n)E_l(\omega_o)+\cdots$$

- Linear polarization

$$P_i^{(1)}(\omega_m) = \frac{\partial U}{\partial E_i^*(\omega_m)} = \epsilon_0\sum_j \chi_{ij}^{(1)}(\omega_m)E_j(\omega_m)$$

- Nonlinear polarization

$$P_i(\omega_n+\omega_m) = \epsilon_0\sum_{jk}\sum_{(nm)}\chi_{ijk}^{(2)}(\omega_n+\omega_m,\omega_n,\omega_m)E_j(\omega_n)E_k(\omega_m). \tag{1.3.12}$$

$$P_i^{(2)}(\omega_m+\omega_n) = \epsilon_0\sum_{jk}\sum_{mn}\chi_{ijk}^{(2)\prime}(-\omega_n-\omega_m;\omega_m,\omega_n)E_j(\omega_m)E_k(\omega_n)$$

$$P_i^{(3)}(\omega_m+\omega_n+\omega_o) = \epsilon_0\sum_{jkl}\sum_{mno}\chi_{ijk}^{(3)\prime}(-\omega_m-\omega_n-\omega_o;\omega_m,\omega_n,\omega_o)E_j(\omega_m)E_k(\omega_n)\,E_l(\omega_o)$$

Sign of first frequency

$$P_i(\omega_3) = \epsilon_0\sum_{jk}[\chi_{ijk}^{(2)}(\omega_3,\omega_1,\omega_2)E_j(\omega_1)E_k(\omega_2)$$
$$+\chi_{ijk}^{(2)}(\omega_3,\omega_2,\omega_1)E_j(\omega_2)E_k(\omega_1)]. \tag{1.3.13}$$

- $\chi^{(n)\prime}$ possesses full permutation symmetry, so $\chi^{(n)}$ does.

Supple : calculate the polarization

- Linear polarization

$$\frac{\partial E_i^*(\omega_m)}{\partial E_i^*(\omega_m)}, \frac{\partial E_j^*(\omega_m)}{\partial E_i^*(\omega_m)}$$

$$P_i^{(1)}(\omega_m) = \frac{\partial U}{\partial E_i^*(\omega_m)} = \frac{\partial}{\partial E_i^*(\omega_m)} \frac{\epsilon_0}{2} \sum_{ij} \chi_{ij}^{(1)}(\omega_m) E_i^*(\omega_m) E_j(\omega_m) =$$

$$\frac{\epsilon_0}{2} \sum_{ij} \chi_{ij}^{(1)}(\omega_m) E_j(\omega_m) \delta_{ii} + \frac{\epsilon_0}{2} \sum_{ji} \chi_{ji}^{(1)}(\omega_m) E_i(\omega_m) \delta_{ij} = \epsilon_0 \sum_j \chi_{ij}^{(1)}(\omega_m) E_j(\omega_m)$$

- Nonlinear polarization

$$\frac{\partial E_i^*(\omega_m+\omega_n)}{\partial E_i^*(\omega_m+\omega_n)}, \frac{\partial E_j^*(\omega_m)}{\partial E_i^*(\omega_m+\omega_n)}, \frac{\partial E_k^*(\omega_n)}{\partial E_i^*(\omega_m+\omega_n)}$$

$$P_i^{(2)}(\omega_m+\omega_n) = \frac{\partial U}{\partial E_i^*(\omega_m+\omega_n)} = \frac{\partial}{\partial E_i^*(\omega_m+\omega_n)} \frac{\epsilon_0}{3} \sum_{ijk} \sum_{mn} \chi_{ijk}^{(2)'}(-\omega_n-\omega_m;\omega_m,\omega_n) E_i^*(\omega_m+\omega_n) E_j(\omega_m) E_k(\omega_n)$$

$$= \frac{\epsilon_0}{3} \sum_{ijk} \sum_{mn} \chi_{ijk}^{(2)'} \delta_{ii} E_j(\omega_m) E_k(\omega_n)$$

$$+ \frac{\epsilon_0}{3} \sum_{ijk} \sum_{mn} \chi_{ijk}^{(2)'} \delta_{ij} \delta_{m,m+n} E_i(\omega_m+\omega_n) E_k(\omega_n)$$

$$+ \frac{\epsilon_0}{3} \sum_{ijk} \sum_{mn} \chi_{ijk}^{(2)'} \delta_{ik} \delta_{n,m+n} E_i(\omega_m+\omega_n) E_j(\omega_m)$$

Kleinman's Symmetry

- ***Nonresonant case under the low-frequency excitation***
  - Quite often, in nonlinear optical interactions
    - Optical waves (ω_i) are much smaller than the lowest resonance frequency of material system
    - Susceptibility is essentially ***independent of frequency***

$$\chi^{(2)}(\omega_1+\omega_2;\omega_1,\omega_2) \approx \frac{e^3}{\epsilon_0 m^2 \omega_0^4 d^4}$$

  - The system responds instantaneously to the applied field

$$\tilde{P}(t) = \epsilon_0 \chi^{(2)} \tilde{E}^2(t)$$

  - Full permutation symmetry is valid under our circumstances

$$\begin{aligned}\chi_{ijk}^{(2)}(\omega_3=\omega_1+\omega_2) &= \chi_{jki}^{(2)}(\omega_1=-\omega_2+\omega_3) = \chi_{kij}^{(2)}(\omega_2=\omega_3-\omega_1)\\ &= \chi_{ikj}^{(2)}(\omega_3=\omega_2+\omega_1) = \chi_{kji}^{(2)}(\omega_2=-\omega_1+\omega_3)\\ &= \chi_{jik}^{(2)}(\omega_1=\omega_3-\omega_2).\end{aligned}$$

  - But, susceptibility doesn't depend on the frequencies

$$\begin{aligned}\chi_{ijk}^{(2)}(\omega_3=\omega_1+\omega_2) &= \chi_{jki}^{(2)}(\omega_3=\omega_1+\omega_2) = \chi_{kij}^{(2)}(\omega_3=\omega_1+\omega_2)\\ &= \chi_{ikj}^{(2)}(\omega_3=\omega_1+\omega_2) = \chi_{jik}^{(2)}(\omega_3=\omega_1+\omega_2)\\ &= \chi_{kji}^{(2)}(\omega_3=\omega_1+\omega_2).\end{aligned}$$

Kleinman symmetry condition : no dispersion of the susceptibility

Contracted Notation

- ***Introducing notation when the Kleinman symmetry condition is valid***

  - The tensor

    Just convention

$$d_{ijk} = \frac{1}{2}\chi^{(2)}_{ijk}$$

  - Nonlinear polarization

$$P_i(\omega_n + \omega_m) = \epsilon_0 \sum_{jk} \sum_{(nm)} 2d_{ijk} E_j(\omega_n) E_k(\omega_m)$$

  - Assuming that d_{ijk} is symmetric in its last two indices
    - ◆ Valid whenever Kleinman's symmetry condition is valid
    - ◆ Generally, it is valid for SHG

jk:	11	22	33	23, 32	31, 13	12, 21
l:	1	2	3	4	5	6

  - Nonlinear susceptibility tensor : (3×6) matrix

$$d_{il} = \begin{bmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{bmatrix}$$

Contracted Notation

- ***Introducing notation when the Kleinman symmetry condition is valid***

$$\begin{array}{lcccccc} jk: & 11 & 22 & 33 & 23, 32 & 31, 13 & 12, 21 \\ l: & 1 & 2 & 3 & 4 & 5 & 6 \end{array}$$

$$d_{il} = \begin{bmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{bmatrix}$$

- Not all of the 18 elements are independent under the Kleinman symmetry condition

$$d_{12} \equiv d_{122} = d_{212} \equiv d_{26}, \qquad d_{14} \equiv d_{123} = d_{213} \equiv d_{25}$$

$$d_{il} = \begin{bmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{16} & d_{22} & d_{23} & d_{24} & d_{14} & d_{12} \\ d_{15} & d_{24} & d_{33} & d_{23} & d_{13} & d_{14} \end{bmatrix}$$

Only 10 independent elements

- The nonlinear polarization leading to SHG

$$\begin{bmatrix} P_x(2\omega) \\ P_y(2\omega) \\ P_z(2\omega) \end{bmatrix} = 2\epsilon_0 \begin{bmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{bmatrix} \begin{bmatrix} E_x(\omega)^2 \\ E_y(\omega)^2 \\ E_z(\omega)^2 \\ 2E_y(\omega)E_z(\omega) \\ 2E_x(\omega)E_z(\omega) \\ 2E_x(\omega)E_y(\omega) \end{bmatrix}$$

Contracted Notation

- ***Introducing notation when the Kleinman symmetry condition is valid***
  - The nonlinear polarization leading to SFG $(\omega_3 = \omega_1 + \omega_2)$

$$\begin{bmatrix} P_x(\omega_3) \\ P_y(\omega_3) \\ P_z(\omega_3) \end{bmatrix} = 4\epsilon_0 \begin{bmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{bmatrix} \begin{bmatrix} E_x(\omega_1)E_x(\omega_2) \\ E_y(\omega_1)E_y(\omega_2) \\ E_z(\omega_1)E_z(\omega_2) \\ E_y(\omega_1)E_z(\omega_2) + E_z(\omega_1)E_y(\omega_2) \\ E_x(\omega_1)E_z(\omega_2) + E_z(\omega_1)E_x(\omega_2) \\ E_x(\omega_1)E_y(\omega_2) + E_y(\omega_1)E_x(\omega_2) \end{bmatrix}$$

Effective Value

Midwinter, J.E., Warner, J., 1965. Br. J. Appl. Phys. 16, 1135.

- ***Nonlinear polarization for a fixed geometry (propagation direction and polarization)***
  - It is possible to express the nonlinear polarization (SFG and SHG)

$$P(\omega_3) = 4\epsilon_0 d_{eff} E(\omega_1) E(\omega_2)$$

$$P(2\omega) = 2\epsilon_0 d_{eff} E(\omega)^2$$

$$P(\omega) = |\boldsymbol{P}(\omega)|$$
$$E(\omega) = |\boldsymbol{E}(\omega)|$$

  - d_{eff} is obtained by determining $\boldsymbol{P}(\omega)$ in matrix equation and then calculating its norm $P(\omega) = |\boldsymbol{P}(\omega)|$
  - For example, negative uniaxial of crystal class 3m (as type II condition)

Table 1

Phase matching condition

	Positive uniaxial	Negative uniaxial
Type I	$f_1 \equiv$ e ray, $f_2 \equiv$ e ray, $f_3 \equiv$ o ray	$f_1 \equiv$ o ray, $f_2 \equiv$ o ray, $f_3 \equiv$ e ray
	$P(\omega_3) = F_1(\theta, \phi, \mathbf{d})\, E(\omega_1)\, E(\omega_2)$	$P(\omega_3) = F_2(\theta, \phi, \mathbf{d})\, E(\omega_1)\, E(\omega_2)$
	$n_3^{\text{ord}} = \frac{f_1}{f_3} n_1^{\text{ext}} + \frac{f_2}{f_3} n_2^{\text{ext}}$	$n_3^{\text{ext}} = \frac{f_1}{f_3} n_1^{\text{ord}} + \frac{f_2}{f_3} n_2^{\text{ord}}$
Type II	$f_1 \equiv$ o ray, $f_2 \equiv$ e ray, $f_3 \equiv$ o ray	$f_1 \equiv$ e ray, $f_2 \equiv$ o ray, $f_3 \equiv$ e ray
	$P(\omega_3) = F_2(\theta, \phi, \mathbf{d})\, E(\omega_1)\, E(\omega_2)$	$P(\omega_3) = F_1(\theta, \phi, \mathbf{d})\, E(\omega_1)\, E(\omega_2)$
	$n_3^{\text{ord}} = \frac{f_1}{f_3} n_1^{\text{ord}} + \frac{f_2}{f_3} n_2^{\text{ext}}$	$n_3^{\text{ext}} = \frac{f_1}{f_3} n_1^{\text{ext}} + \frac{f_2}{f_3} n_2^{\text{ord}}$

$f_3 = f_2 + f_1$ and $f_3 > f_2 \geqslant f_1$. We assume that $dn/d\lambda \leqslant 0$ throughout the range from f_1 to f_3.

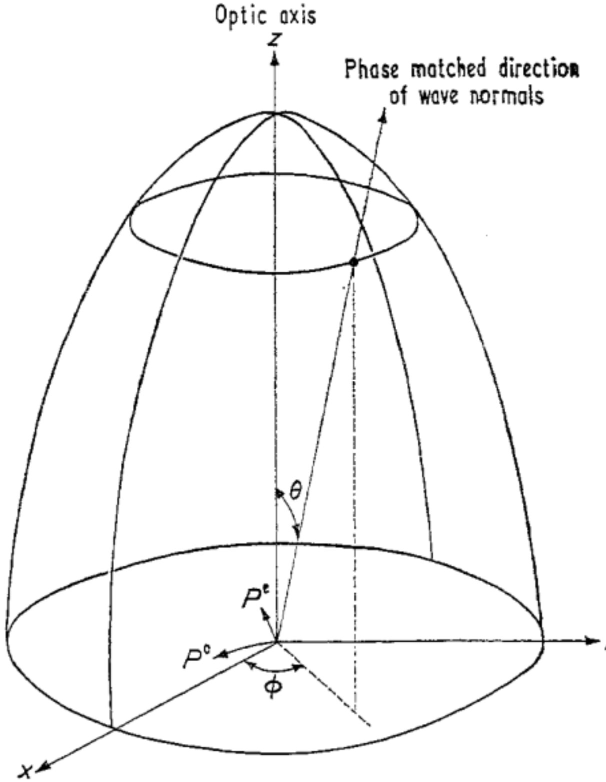
Table 3

Class	$F_1(\theta, \phi, \mathbf{d})$	$F_2(\theta, \phi, \mathbf{d})$
$\bar{6}2m$	$+ d_{22} \cos^2\theta \cos 3\phi$	$- d_{22} \cos\theta \sin 3\phi$
$6mm$	0	$+ d_{15} \sin\theta$
622	0	0
$\bar{6}$	$\cos^2\theta\,(d_{11} \sin 3\phi + d_{22} \cos 3\phi)$	$\cos\theta\,(d_{11} \cos 3\phi - d_{22} \sin 3\phi)$
6	0	$+ d_{15} \sin\theta$
$3m$	$d_{22} \cos^2\theta \cos 3\phi$	$d_{15} \sin\theta - d_{22} \cos\theta \sin 3\phi$
32	$d_{11} \cos^2\theta \sin 3\phi$	$d_{11} \cos\theta \cos 3\phi$
3	$\cos^2\theta\,(d_{11} \sin 3\phi + d_{22} \cos 3\phi)$	$d_{15} \sin\theta + \cos\theta\,(d_{11} \cos 3\phi - d_{22} \sin 3\phi)$
$\bar{4}2m$	$+ d_{14} \sin 2\theta \cos 2\phi$	$- d_{14} \sin\theta \sin 2\phi$
$4mm$	0	$+ d_{15} \sin\theta$
422	0	0
$\bar{4}$	$\sin 2\theta\,(d_{14} \cos 2\phi - d_{15} \sin 2\phi)$	$- \sin\theta\,(d_{14} \sin 2\phi + d_{15} \cos 2\phi)$
4	0	$+ d_{15} \sin\theta$

Effective Value

Midwinter, J.E., Warner, J., 1965. Br. J. Appl. Phys. 16, 1135.

- ***Nonlinear polarization for a fixed geometry (propagation direction and polarization)***
  - For example, negative uniaxial of crystal class 3m (as type II condition)
    - ◆ $d_{eff} = d_{22} \cos^2 \theta \cos 3\phi$



◆ *θ : the angle between the propagation vector and the crystalline z axis (the optic axis)*

◆ *ϕ : the azimuthal angle between the crystalline x axis and the projection for the propagation vector onto the xz crystalline plane*

Spatial Symmetry of Nonlinear Medium

- ***Fourfold axis of symmetry***
  - The linear and nonlinear susceptibility tensors are constrained by the symmetry properties of the optical medium.
    - ◆ Consider a crystal for which the x and y directions are equivalent but for which the z direction is different

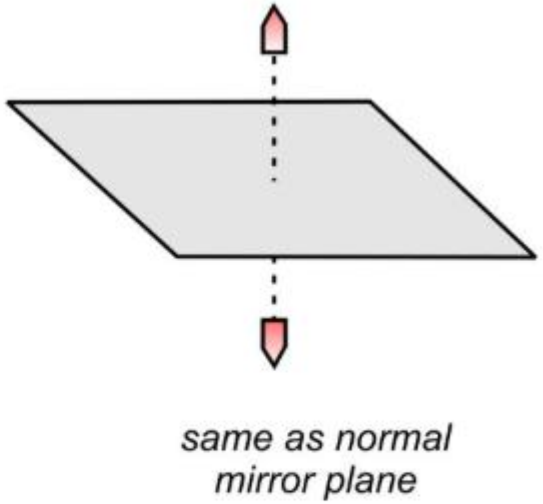
$$\chi_{zxx}^{(2)} = \chi_{zyy}^{(2)}$$

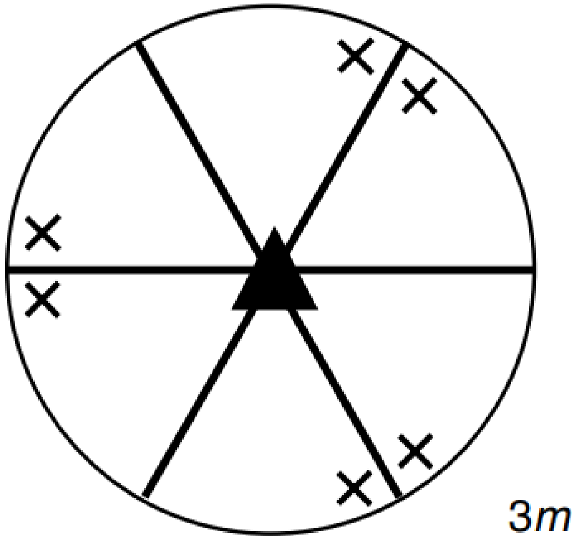
  - If the crystal were rotated by 90 degrees about the z axis, crystal structure would look identical.

- ***Nonlinear polarization for a fixed geometry (propagation direction and polarization)***
  - The linear and nonlinear optical susceptibilities
    - ◆ determined by symmetry properties
  - What types of symmetry properties can occur in a crystalline medium
    - ◆ mathematical method (group theory)

Spatial Symmetry of Nonlinear Medium

- ***Crystal Classification by group theory***
  - 32 possible crystal classes depending on the point group symmetry of the crystal
    - Fourfold axis of symmetry : ***point group 4***
    - Three-fold axis of symmetry and a plane of mirror symmetry parallel to this axis : ***point group 3m***





R. Ballou, *Crystallography: Symmetry groups and group representations*, Eur. Phys. J. Conf. 22, 00006 (2012).

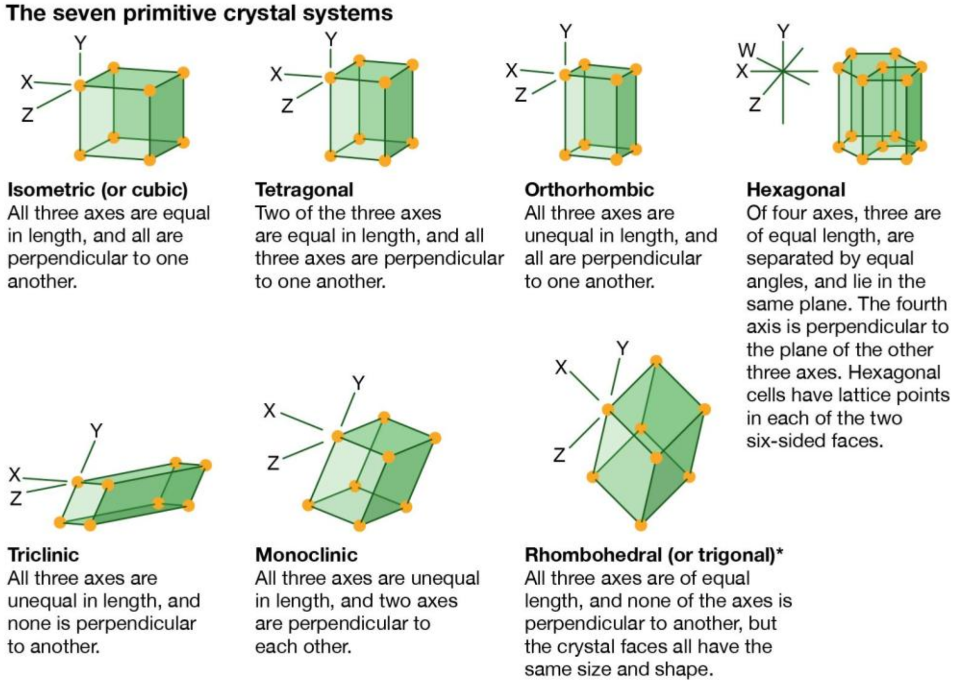
https://opengeology.org/Mineralogy/10-crystal-morphology-and-symmetry/

Influence of Spatial Symmetry

- ***Considering symmetry imposes on the linear susceptibility tensor***
  - Five difference cases by a group theorical analysis
  - Isotropic materials are also included in below table

Triclinic	$\begin{bmatrix} xx & xy & xz \\ yx & yy & yz \\ zx & zy & zz \end{bmatrix}$
Monoclinic	$\begin{bmatrix} xx & 0 & xz \\ 0 & yy & 0 \\ zx & 0 & zz \end{bmatrix}$
Orthorhombic	$\begin{bmatrix} xx & 0 & 0 \\ 0 & yy & 0 \\ 0 & 0 & zz \end{bmatrix}$
Tetragonal Trigonal Hexagonal	$\begin{bmatrix} xx & 0 & 0 \\ 0 & xx & 0 \\ 0 & 0 & zz \end{bmatrix}$
Cubic Isotropic	$\begin{bmatrix} xx & 0 & 0 \\ 0 & xx & 0 \\ 0 & 0 & xx \end{bmatrix}$

Biaxial crystals



- Isotropic crystal : only diagonal with equal diagonal components
- Anisotropic crystal : polarization needs not to parallel to E-field (Birefringence)
- Tetragonal, Trigonal, Hexagonal crystal : uniaxial crystals

$$\frac{x^2 + y^2}{n_o^2} + \frac{z^2}{n_e^2} = 1$$

Rotational symmetry

Influence of Spatial Symmetry

- ***Crystals are categorized seven possible crystal systems***
  - 32 point group

Crystal System	Crystal Class	Nonvanishing Tensor Elements
Triclinic	$1 = C_1$	All elements are independent and nonzero
	$\bar{1} = S_2$	Each element vanishes
Monoclinic	$2 = C_2$	$xyz, xzy, xxy, xyx, yxx, yyy, yzz, yzx, yxz, zyz, zzy, zxy, zyx$ (twofold axis parallel to $\hat{y}$)
	$m = C_{1h}$	$xxx, xyy, xzz, xzx, xxz, yyz, yzy, yxy, yyx, zxx, zyy, zzz, zzx, zxz$ (mirror plane perpendicular to $\hat{y}$)
	$2/m = C_{2h}$	Each element vanishes
Orthorhombic	$222 = D_2$	$xyz, xzy, yzx, yxz, zxy, zyx$
	$mm2 = C_{2v}$	$xzx, xxz, yyz, yzy, zxx, zyy, zzz$
	$mmm = D_{2h}$	Each element vanishes
Tetragonal	$4 = C_4$	$xyz = -yxz, xzy = -yzx, xzx = yzy, xxz = yyz, zxx = zyy, zzz, zxy = -zyx$
	$\bar{4} = S_4$	$xyz = yxz, xzy = yzx, xzx = -yzy, xxz = -yyz, zxx = -zyy, zxy = zyx$
	$422 = D_4$	$xyz = -yxz, xzy = -yzx, zxy = -zyx$
	$4mm = C_{4v}$	$xzx = yzy, xxz = yyz, zxx = zyy, zzz$
	$\bar{4}2m = D_{2d}$	$xyz = yxz, xzy = yzx, zxy = zyx$
	$4/m = C_{4h}$	Each element vanishes
	$4/mmm = D_{4h}$	Each element vanishes
Cubic	$432 = O$	$xyz = -xzy = yzx = -yxz = zxy = -zyx$
	$\bar{4}3m = T_d$	$xyz = xzy = yzx = yxz = zxy = zyx$
	$23 = T$	$xyz = yzx = zxy, xzy = yxz = zyx$
	$m3 = T_h, m3m = O_h$	Each element vanishes
Trigonal	$3 = C_3$	$xxx = -xyy = -yyz = -yxy, xyz = -yxz, xzy = -yzx, xzx = yzy, xxz = yyz, yyy = -yxx = -xxy = -xyx, zxx = zyy, zzz, zxy = -zyx$
	$32 = D_3$	$xxx = -xyy = -yyx = -yxy, xyz = -yxz, xzy = -yzx, zxy = -zyx$
	$3m = C_{3v}$	$xzx = yzy, xxz = yyz, zxx = zyy, zzz, yyy = -yxx = -xxy = -xyx$ (mirror plane perpendicular to $\hat{x}$)
	$\bar{3} = S_6, \bar{3}m = D_{3d}$	Each element vanishes
Hexagonal	$6 = C_6$	$xyz = -yxz, xzy = -yzx, xzx = yzy, xxz = yyz, zxx = zyy, zzz, zxy = -zyx$
	$\bar{6} = C_{3h}$	$xxx = -xyy = -yxy = -yyx, yyy = -yxx = -xyx = -xxy$
	$622 = D_6$	$xyz = -yxz, xzy = -yxz, zxy = -zyx$
	$6mm = C_{6v}$	$xzx = yzy, xxz = yyz, zxx = zyy, zzz$
	$\bar{6}m2 = D_{3h}$	$yyy = -yxx = -xxy = -xyx$
	$6/m = C_{6h}$	Each element vanishes
	$6/mmm = D_{6h}$	Each element vanishes

Influence of Spatial Symmetry (Nonlinear Response)

- ***Centrosymmetry (inversion symmetry)***
  - $\chi^{(2)}$ must vanish
  - 11 of the 32 crystal classes : inversion symmetry

- ***Proof why inversion symmetry vanish second-order susceptibility***
  - Assuming medium that responds instantaneously to the applied optical field

$$\boxed{\tilde{P}(t) = \epsilon_0 \chi^{(2)} \tilde{E}^2(t)}$$

$$\tilde{E}(t) = \mathcal{E} \cos \omega t$$

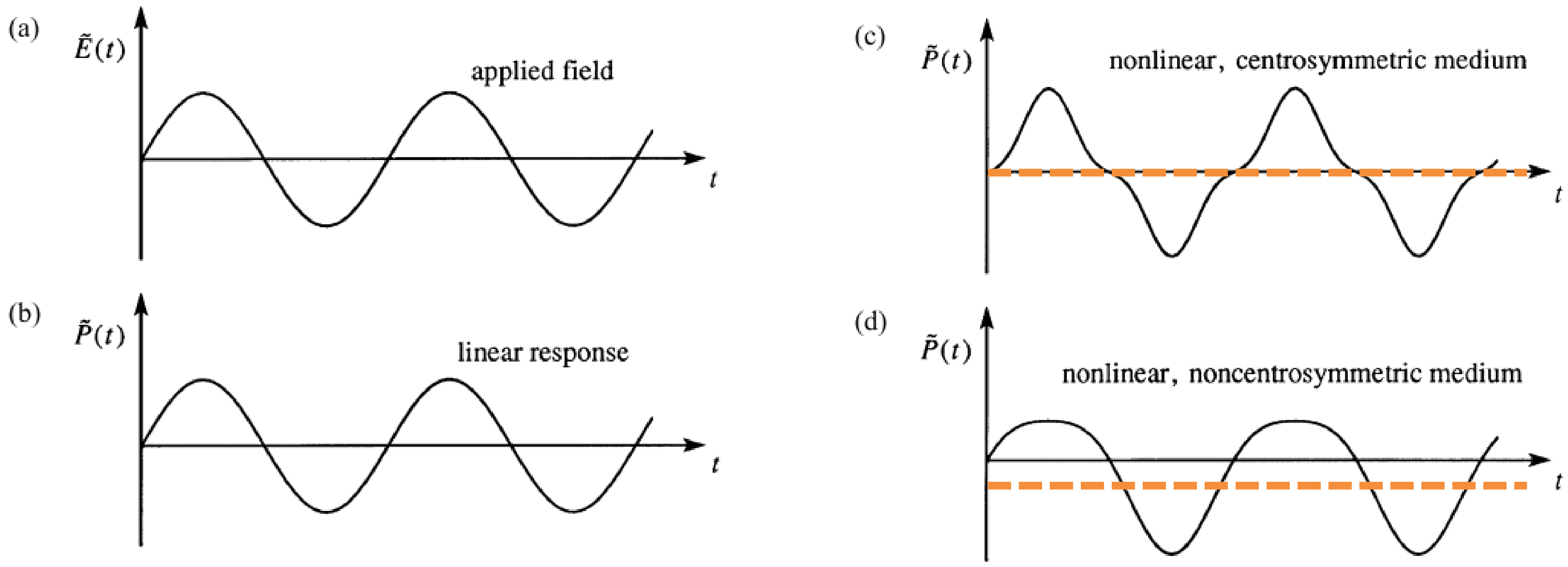
Must be same : $\chi^{(2)} = 0$

  - $\tilde{E}(t) \rightarrow -\tilde{E}(t)$, then $\tilde{P}(t) \rightarrow -\tilde{P}(t)$ by inversion symmetry

$$\boxed{-\tilde{P}(t) = \epsilon_0 \chi^{(2)} \left[-\tilde{E}(t)\right]^2}$$

Influence of Spatial Symmetry (Nonlinear Response)

- ***Intuitively by considering the motion of an electron in a nonparabolic potential well***
  - (b) : no distortion
  - (c) : odd harmonics; time-averaged response is zero $\tilde{F}_{restoring} = -m\omega_0^2\tilde{x} - mb\tilde{x}^3$
  - (d) : even and odd harmonics; time-averaged response is not zero $\tilde{F}_{restoring} = -m\omega_0^2\tilde{x} - mb\tilde{x}^2$



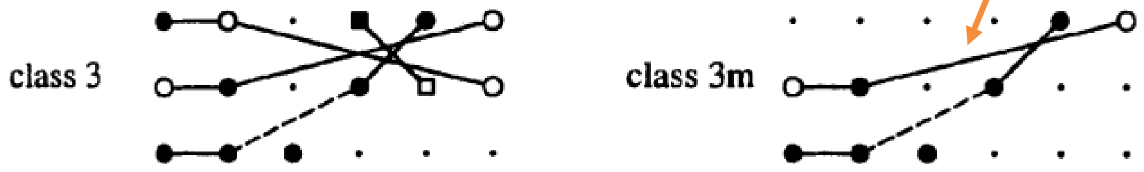
Influence of Spatial Symmetry (Nonlinear Susceptibility)

- ***For example, here's a crystal of class 3m***
  - d_{il} matrix

$$d_{il} = \begin{bmatrix} 0 & 0 & 0 & 0 & d_{31} & -d_{22} \\ -d_{22} & d_{22} & 0 & d_{31} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{bmatrix}$$

Uniaxial crystal classes

Kleinman symmetry is also involved



  - Caution : considerable spread in the values of the nonlinear coefficients
    - ◆ Because of the wavelength dependence of the nonlinear and measurement inaccuracies

Material	Point Group	d_{il} (pm/V)
Ag_3AsS_3 (proustite)	$3m = C_{3v}$	$d_{22} = 18$ $d_{15} = 11$
$AgGaSe_2$	$\bar{4}2m = D_{2d}$	$d_{36} = 33$
$AgSbS_3$ (pyrargyrite)	$3m = C_{3v}$	$d_{15} = 8$ $d_{22} = 9$
beta-BaB_2O_4 (BBO) (beta barium borate)	$3m = C_{3v}$	$d_{22} = 2.2$
$CdGeAs_2$	$\bar{4}2m = D_{2d}$	$d_{36} = 235$
CdS	$6mm = C_{6v}$	$d_{33} = 78$ $d_{31} = -40$
GaAs	$\bar{4}3m$	$d_{36} = 370$
KH_2PO_4 (KDP)	$2m$	$d_{36} = 0.43$
KD_2PO_4 (KD*P)	$2m$	$d_{36} = 0.42$
$LiIO_3$	$6 = C_6$	$d_{15} = -5.5$ $d_{31} = -7$
$LiNbO_3$	$3m = C_{3v}$	$d_{32} = -30$ $d_{31} = -5.9$
Quartz	$32 = D_3$	$d_{11} = 0.3$ $d_{14} = 0.008$

Number of Independent Elements of Susceptibility

- ***How to reduce the elements***

  - (1) for describing mutual interaction of three optical waves

    324

  - (2) Physical fields (polarization, E-field) are real

    162

  - (3) Intrinsic permutation symmetry (about input fields)

    81

  - (4) lossless medium (real susceptibility) and full permutation symmetry

    27

  - (4) For SHG

    18

  - (4) Kleinman's symmetry (low-frequency excitation)

    10

$\omega_3 = \omega_1 + \omega_2$

Frequency indices + E-field indices : simultaneously

Noncentrosymmetric and Cubic Crystal Classes

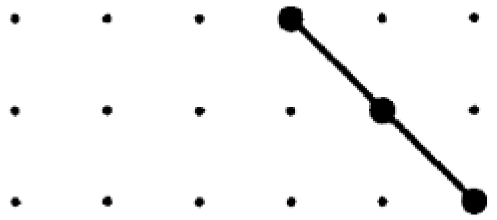
- ***A material can possess a cubic lattice and be noncentrosymmetric***
  - Gallium arsenide : structure as the zincblende
  - Its point group $\bar{4}3m$: nonvanishing second-order nonlinear optical response
  - Cubic lattice : Gallium arsenide doesn’t display birefringence
- ***Hard phase-matching***
  - Birefringence is commonly used to achieve phase-matching
  - But cubic lattice is isotropic, it is too hard to achieve it

$\bar{4}3m = \boxed{T_d}$

Tetrahedral

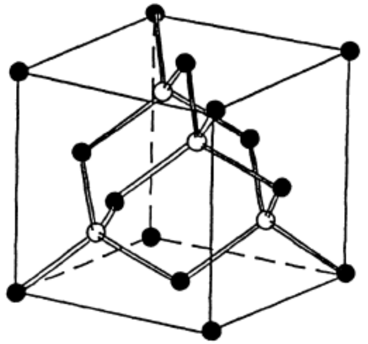
$$xyz = xzy = yzx = yxz = zxy = zyx$$

classes
$\bar{4}3$m
and 23



Not zero

(b) zincblende structure

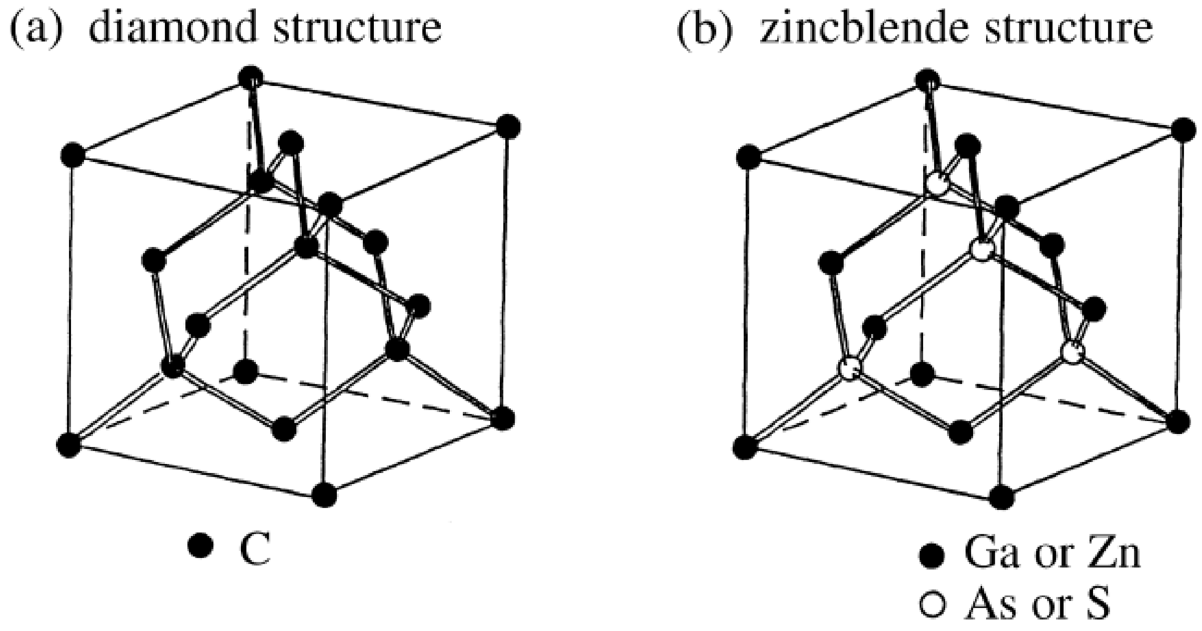


● Ga or Zn
○ As or S

cubic lattice (isotropic)

Noncentrosymmetric and Cubic Crystal Classes

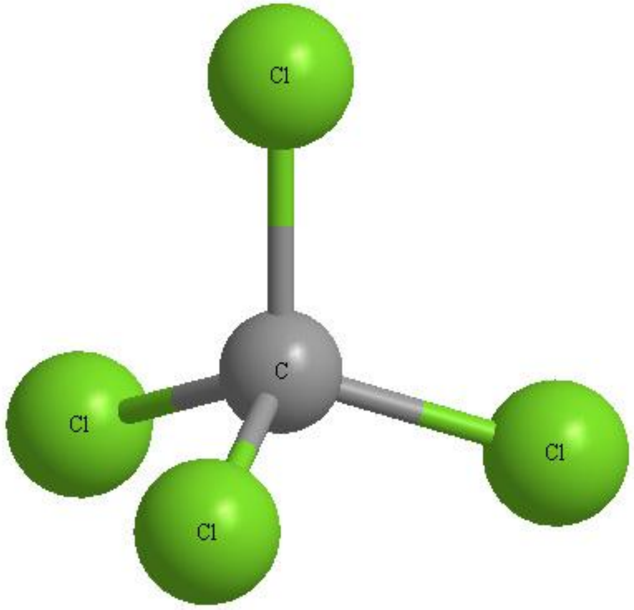
- ***Different nearest-neighbors give different characteristic***
  - Diamond structure : cubic lattice and centrosymmetric $\chi^{(2)} = 0$
  - Zincblende structure : cubic lattice and noncentrosymmetric $\chi^{(2)} \neq 0$



Noncentrosymmetric and Polar Crystal Classes

- ***Restrict condition that possess a nonzero second-order susceptibility***
  - Certain crystal possess a permanent dipole moment
    - ***Polar crystals, ferroelectric crystals***
  - They can display the ***pyroelectric effect*** and photorefractive effect
    - A change of permanent dipole moment with temperature
    - which can be used to construct optical detector
  - Ferroelectric crystals within group theoretical arguments

$$\begin{array}{ccccc} 1 & 2 & 3 & 4 & 6 \\ m & mm2 & 3m & 4mm & 6mm \end{array}$$



Always Yes!

Polar crystals $\rightleftarrows$ **Noncentrosymmetric crystal**

Always No!

- For example, $\mathrm{CCl_4}$ cannot posses a permanent dipole moment. But it is noncentrosymmetric

Third Order Nonlinear Response

Isotropic

There are 21 nonzero elements, of which only 3 are independent. They are:

$$yyzz = zzyy = zzxx = xxzz = xxyy = yyxx, \tag{1.5.38}$$
$$yzyz = zyzy = zxzx = xzxz = xyxy = yxyx, \tag{1.5.39}$$
$$yzzy = zyyz = zxxz = xzzx = xyyx = yxxy; \tag{1.5.40}$$

and

$$xxxx = yyyy = zzzz = xxyy + xyxy + xyyx.$$

Cubic

For the two classes 23 and $m3$, there are 21 nonzero elements, of which only 7 are independent. They are:

$$xxxx = yyyy = zzzz, \tag{1.5.41}$$
$$yyzz = zzxx = xxyy, \tag{1.5.42}$$
$$zzyy = xxzz = yyxx, \tag{1.5.43}$$
$$yzyz = zxzx = xyxy, \tag{1.5.44}$$
$$zyzy = xzxz = yxyx, \tag{1.5.45}$$
$$yzzy = zxxz = xyyx, \tag{1.5.46}$$
$$zyyz = xzzx = yxxy. \tag{1.5.47}$$

For the three classes 432, $\bar{4}3m$, and $m3m$, there are 21 nonzero elements, of which only 4 are independent. They are:

$$xxxx = yyyy = zzzz, \tag{1.5.48}$$
$$yyzz = zzyy = zzxx = xxzz = xxyy = yyxx, \tag{1.5.49}$$
$$yzyz = zyzy = zxzx = xzxz = xyxy = yxyx, \tag{1.5.50}$$
$$yzzy = zyyz = zxxz = xzzx = xyyx = yxxy. \tag{1.5.51}$$

Hexagonal

For the three classes 6, $\bar{6}$, and $6/m$, there are 41 nonzero elements, of which only 19 are independent. They are:

$$\begin{array}{c} zzzz, \\ xxxx = yyyy = xxyy + xyyx + xyxy, \end{array} \quad \begin{cases} xxyy = yyxx, \\ xyyx = yxxy, \\ xyxy = yxyx, \end{cases}$$

$$\begin{array}{ll} yyzz = xxzz, & xyzz = -yxzz, \\ zzyy = zzxx, & zzxy = -zzyx, \\ zyyz = zxxz, & zxyz = -zyxz, \\ yzzy = xzzx, & xzzy = -yzzx, \\ yzyz = xzxz, & xzyz = -yzxz, \\ zyzy = zxzx, & zxzy = -zyzx, \end{array}$$

$$xxxy = -yyyx = yyxy + yxyy + xyyy, \quad \begin{cases} yyxy = -xxyx, \\ yxyy = -xyxx, \\ xyyy = -yxxx. \end{cases}$$

Pass

Time-Domain Description of Optical Linearities

- ***Describing optical nonlinearities directly in the time domain***
  - Sometimes more convenient than frequency domain (Short pulse applied field)
  - Frequency domain is useful when input field is nearly monochromatic

- ***A purely linear response*** $(\boldsymbol{t}' > \boldsymbol{t})$

$$\tilde{P}^{(1)}(t) = \epsilon_0 \int_{-\infty}^{t} R^{(1)}(t'-t)\tilde{E}(t')dt' = \epsilon_0 \int_{0}^{\infty} R^{(1)}(\tau)\tilde{E}(t-\tau)d\tau$$

  - $R^{(1)}(\tau)$: linear response function
    - ◆ Contribution to the polarization produced at time t by an E-field applied at earlier time $t-\tau$
  - Low limit of integration is 0 by ***causality :*** $\tilde{P}^{(1)}(t)$ depends only on past
  - Transformed to the frequency domain (FT)

$$E(\omega) = \int_{-\infty}^{\infty} \tilde{E}(t)e^{i\omega t}dt$$

$$\tilde{E}(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} E(\omega)e^{-i\omega t}d\omega$$

Time-Domain Description of Optical Linearities

- ***FT of the polarization & linear susceptibility***

$$\tilde{P}^{(1)}(t) = \frac{\epsilon_0}{2\pi}\int_0^\infty d\tau \int_{-\infty}^{\infty} R^{(1)}(\tau)E(\omega)e^{-i\omega(t-\tau)}d\omega = \frac{\epsilon_0}{2\pi}\int_{-\infty}^{\infty} d\omega \left[\int_{-0}^{\infty} d\tau R^{(1)}(\tau)e^{i\omega\tau}\right] E(\omega)e^{-i\omega t}$$

$$\tilde{P}^{(1)}(t) = \frac{\epsilon_0}{2\pi}\int_{-\infty}^{\infty} d\omega\, \chi^{(1)}(\omega;\omega)E(\omega)e^{-i\omega t}$$

  - Polarization of linear response

$$\tilde{P}^{(1)}(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega \left[\epsilon_0\chi^{(1)}(\omega;\omega)E(\omega)\right]e^{-i\omega t} = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega\, P(\omega)e^{-i\omega t}$$

Time-Domain Description of Optical Nonlinearities

- ***FT of Second-order response function***

$$\tilde{P}^{(2)}(t) = \epsilon_0 \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 R^{(2)}(\tau_1, \tau_2)\tilde{E}(t-\tau_1)\tilde{E}(t-\tau_2)$$

- $R^{(2)}(\tau_1 - \tau_2) = 0$ if either τ_1 or τ_1 is negative $\qquad \omega_\sigma = \omega_1 + \omega_2$

$$\tilde{P}^{(2)}(t) = \int_{-\infty}^\infty \frac{d\omega_1}{2\pi} \int_{-\infty}^\infty \frac{d\omega_2}{2\pi} \epsilon_0 \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 R^{(2)}(\tau_1, \tau_2) E(\omega_1) e^{-i\omega_1(t-\tau_1)} E(\omega_2) e^{-i\omega_2(t-\tau_2)}$$

$$= \epsilon_0 \int_{-\infty}^\infty \frac{d\omega_1}{2\pi} \int_{-\infty}^\infty \frac{d\omega_2}{2\pi} \left[\int_0^\infty d\tau_1 \int_0^\infty d\tau_2 R^{(2)}(\tau_1, \tau_2) e^{-i\omega_1\tau_1} e^{-i\omega_2\tau_2}\right] E(\omega_1)E(\omega_2)e^{-i\omega_\sigma t}$$

$$= \epsilon_0 \int_{-\infty}^\infty \frac{d\omega_1}{2\pi} \int_{-\infty}^\infty \frac{d\omega_2}{2\pi} \chi^{(2)}(\omega_\sigma; \omega_1, \omega_2) E(\omega_1)E(\omega_2)e^{-i\omega_\sigma t}$$

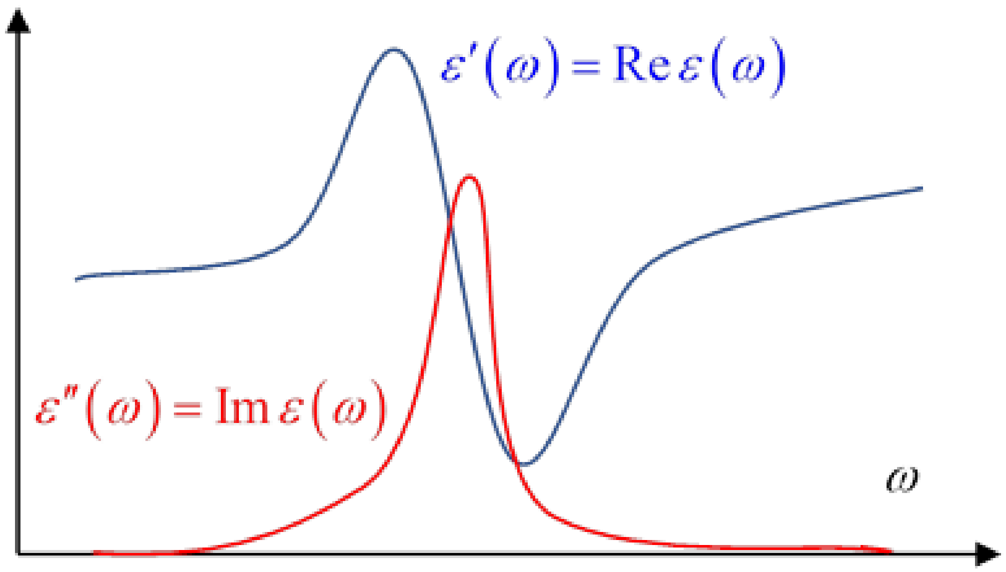
- ***Third-order***

$$\tilde{P}^{(3)}(t) = \epsilon_0 \int_{-\infty}^\infty \frac{d\omega_1}{2\pi} \int_{-\infty}^\infty \frac{d\omega_2}{2\pi} \int_{-\infty}^\infty \frac{d\omega_3}{2\pi} \chi^{(3)}(\omega_\sigma; \omega_1, \omega_2, \omega_3) \times E(\omega_1)E(\omega_2)E(\omega_3)e^{-i\omega_\sigma t},$$

$$\chi^{(3)}(\omega_\sigma; \omega_1, \omega_2, \omega_3) = \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 \times R^{(3)}(\tau_1, \tau_2, \tau_3)\, e^{i(\omega_1\tau_1 + \omega_2\tau_2 + \omega_3\tau_3)}.$$

Kramers-Kronig Relation

- ***Kramers-Kronig (KK) relations***
  - These condition relate real and imaginary parts of frequency-dependent quantities
  - A knowledge of the frequency dependence of the imaginary part → the real part of the susceptibility at some frequency
  - Measuring an absorption spectrum : easier than to measure the frequency dependence of the refractive index



Kramers-Kronig Relation in Linear Optics

- ***Kramers-Kronig (KK) relations in linear optics***

$$\chi^{(1)}(\omega) \equiv \chi^{(1)}(\omega;\omega) = \int_0^\infty d\tau R^{(1)}(\tau) e^{i\omega\tau}$$

  - $R^{(1)}(\tau) \in \mathbb{R}$: polarization and applied field is real quantities (because E-field and Polarization are real)

$$\chi^{(1)}(-\omega) = \chi^{(1)}(\omega)^*$$

- $\chi(\boldsymbol{\omega})$ ***is analytic (single valued and possessing continuous derivatives)***

  - $\chi(\omega)$ in the upper half of the complex ω plane : $\mathrm{Im}\,\omega \geq 0$

$$\omega = \mathrm{Re}\,\omega + \mathrm{Im}\,\omega$$

$$\int_0^\infty d\tau R^{(1)}(\tau) e^{i[\mathrm{Re}\,\omega + \mathrm{Im}\,\omega]\tau}$$

  - $\mathrm{Im}\,\omega > 0$ for convergence
  - $\mathrm{Im}\,\omega = 0$: $R^{(1)}(\tau)$ must be square integrable; ω is physically measurable quantity

Kramers-Kronig Relation in Linear Optics

- ***Cauchy principal value of the integral***
  - Considering the integral with simple pole

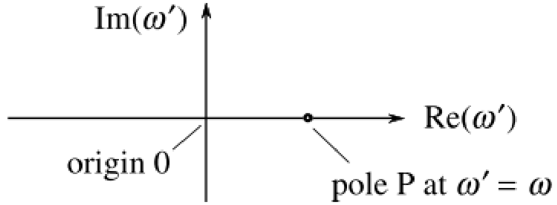
$$\mathrm{Int} = \int_{-\infty}^{\infty} \frac{\chi^{(1)}(\omega')d\omega'}{\omega' - \omega}$$

  - Cauchy principal value of the integral

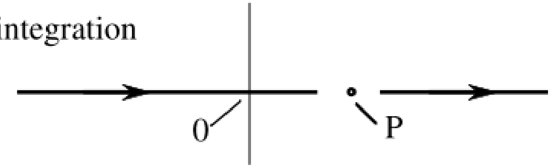
$$\int_{-\infty}^{\infty} \frac{\chi^{(1)}(\omega')\omega'}{\omega' - \omega} \equiv \lim_{\delta \to 0} \left[\int_{-\infty}^{\omega-\delta} \frac{\chi^{(1)}(\omega')d\omega'}{\omega' - \omega} + \int_{\delta+\omega}^{\infty} \frac{\chi^{(1)}(\omega')d\omega'}{\omega' - \omega} \right]$$

  - Desired integral $\mathrm{Int} = \mathrm{Int}\ a - \mathrm{Int}\ b - \mathrm{Int}\ c$

(a) complex ω' plane



(b) desired path of integration



$$\mathrm{Int}\ c = -\frac{i}{\pi}\chi^{(1)}(\omega), \qquad \chi^{(1)}(\omega) = \int_{-\infty}^{\infty} \frac{\chi^{(1)}(\omega')d\omega'}{\omega' - \omega}$$

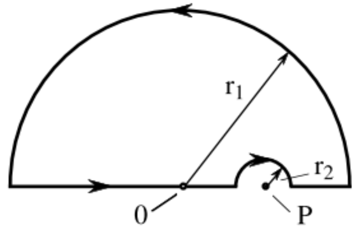
$r_2 \to 0$

Residue theory

$$\oint_\gamma f(z)\, dz = 2\pi i \sum \mathrm{Res}(f, a_k)$$

$$\int_{path\ C} \frac{\chi^{(1)}(\omega')d\omega'}{\omega' - \omega} = \mathrm{Int}C = 2\pi i \chi^{(1)}(\omega')\left(\frac{1}{2}\right)$$

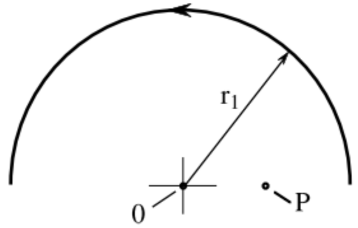
$\mathrm{Int}\ a = 0$: closed path



$\mathrm{Int}\ b = 0$: $|\omega'| \to \infty$

Integrand $\chi^{(1)}(\omega')/|\omega'| \to 0$

Finite response time



Kramers-Kronig Relation in Linear Optics

- ***Cauchy principal value of the integral***
  - $\chi^{(1)}(\omega) = \mathrm{Re}\,\chi^{(1)}(\omega) + i\mathrm{Im}\,\chi^{(1)}(\omega)$

$$\chi^{(1)}(\omega) = -\frac{i}{\pi}\int_{-\infty}^{\infty} \frac{\left[\mathrm{Re}\,\chi^{(1)}(\omega') + i\mathrm{Im}\,\chi^{(1)}(\omega')\right]d\omega'}{\omega' - \omega}$$

$$\mathrm{Re}\,\chi^{(1)}(\omega) = \frac{1}{\pi}\int_{-\infty}^{\infty} \frac{\left[\mathrm{Im}\,\chi^{(1)}(\omega')\right]d\omega'}{\omega' - \omega}, \qquad \mathrm{Im}\,\chi^{(1)}(\omega) = \frac{-1}{\pi}\int_{-\infty}^{\infty} \frac{\left[\mathrm{Re}\,\chi^{(1)}(\omega')\right]d\omega'}{\omega' - \omega}$$

  - It is usually easier to measure absorption spectra than the frequency dependence of the refractive index

Kramers-Kronig Relation in Noninear Optics

- ***Nonlinear Susceptibility***
  - For three input frequencies, $\omega_\sigma = \omega_1 + \omega_2 + \omega_3$

$$\chi^{(3)}(\omega_\sigma; \omega_1, \omega_2, \omega_3) = \frac{1}{i\pi} \int_{-\infty}^{\infty} \frac{\chi^{(3)}(\omega'_\sigma; \omega_1, \omega'_2, \omega_3)}{\omega'_2 - \omega_2} d\omega'_2, \qquad \omega'_\sigma = \omega_1 + \omega'_2 + \omega_3$$

  - Third order nonlinear susceptibility is FT of a causal response function

$$\chi^{(3)}(\omega_\sigma; \omega_1, \omega_2, \omega_3) = \int_0^{\infty} d\tau_1 \int_0^{\infty} d\tau_2 \int_0^{\infty} d\tau_3 \times R^{(3)}(\tau_1, \tau_2, \tau_3)\, e^{i(\omega_1\tau_1 + \omega_2\tau_2 + \omega_3\tau_3)}$$

    - ◆ A function of its three independent frequency
    - ◆ Analytic at $\mathrm{Im}\,\omega_1 \geq 0, \mathrm{Im}\,\omega_2 \geq 0, \mathrm{Im}\,\omega_3 \geq 0$

  - $\chi^{(3)}(\omega_\sigma; \omega_1; \omega_2; \omega_3)E(\omega_1)E(\omega_2)E(\omega_2)$ is linear in the field $E(\omega_2)$
  - And the physical system is causal

KK relation!

Kramers-Kronig Relation in Noninear Optics

- ***Nonlinear Susceptibility***

  - Luan, P. G. (1993). *Kramers–Kronig relations for nonlinear susceptibilities*. **Il Nuovo Cimento D**, *15*(8), 805–817.

$$\hat{\chi}^{(n)}(\Omega_1, \Omega_2, \ldots, \Omega_k, \ldots, \Omega_n) = \frac{1}{\mathrm{i}\pi} \mathscr{P} \int_{-\infty}^{\infty} \frac{\hat{\chi}^{(n)}(\Omega_1, \Omega_2, \ldots, \Omega, \ldots, \Omega_n)}{\Omega - \Omega_k} \mathrm{d}\Omega$$

$$\chi^{(n)}(\omega_1 + p_1\omega, \omega_2 + p_2\omega, \ldots, \omega_n + p_n\omega) = \frac{1}{\mathrm{i}\pi} \mathscr{P} \int_{-\infty}^{\infty} \frac{\chi^{(n)}(\omega_1 + p_1\Omega, \omega_2 + p_2\Omega, \ldots, \omega_n + p_n\Omega)}{\Omega - \omega} \mathrm{d}\Omega$$

$$\chi^{(n)}(\omega_\sigma; \omega_1 + p_1\omega, \omega_2 + p_2\omega, \ldots, \omega_n + p_n\omega) = \frac{1}{i\pi} \int_{-\infty}^{\infty} \frac{\chi^{(n)}(\omega'_\sigma; \omega_1 + p_1\omega', \omega_2 + p_2\omega', \ldots, \omega_n + p_n\omega')}{\omega' - \omega} d\omega'$$

  - ◆ $p_i \geq 0$ and where at least one p_i must be nonzero

  - Second-harmonic generation and third-harmonic generation

$$\chi^{(2)}(2\omega; \omega, \omega) = \frac{1}{i\pi} \int_{-\infty}^{\infty} \frac{\chi^{(2)}(2\omega'; \omega', \omega')}{\omega' - \omega} d\omega' \qquad \chi^{(3)}(3\omega; \omega, \omega, \omega) = \frac{1}{i\pi} \int_{-\infty}^{\infty} \frac{\chi^{(3)}(3\omega'; \omega', \omega', \omega')}{\omega' - \omega} d\omega'.$$

Kramers-Kronig Relation in Noninear Optics

- ***For the change in refractive index(RI) induced by an auxiliary beam (Cannot be represented by KK)***

$$\chi^{(3)}(\omega;\omega,\omega_1,-\omega_1)=\frac{1}{i\pi}\int_{-\infty}^{\infty}\frac{\chi^{(3)}(\omega';\omega',\omega_1,-\omega_1)\,d\omega'}{\omega'-\omega}.$$

- It is not possible to form a KK relation is for the self-induced change in RI ($\chi^{(3)}(\omega';\omega',\omega_1,-\omega_1)$
  - ◆ Third frequency is negative

Kramers-Kronig relations are valid for some but not all nonlinear optical processes