Linear dielectric response and second harmonic generation

Maxwell's Equations to the wave equation

- The induced polarization, **P**, contains the effect of the medium:

$$\vec{\nabla}\cdot\mathbf{E}=0 \qquad \vec{\nabla}\times\mathbf{E}=-\frac{\partial\mathbf{B}}{\partial t}$$

$$\vec{\nabla}\cdot\mathbf{B}=0 \qquad \vec{\nabla}\times\mathbf{B}=\mu_0\frac{\partial\mathbf{D}}{\partial t}$$

Define the displacement vector

$$\mathbf{D}=\varepsilon_0\mathbf{E}+\mathbf{P}$$

- Derive the wave equation:

$$\rightarrow\vec{\nabla}\times\mathbf{B}=\mu_0\frac{\partial\mathbf{D}}{\partial t}=\frac{1}{c^2}\frac{\partial\mathbf{E}}{\partial t}+\mu_0\frac{\partial\mathbf{P}}{\partial t}$$

$$\vec{\nabla}\times\left(\vec{\nabla}\times\mathbf{E}\right)=-\vec{\nabla}\times\frac{\partial\mathbf{B}}{\partial t}=-\frac{\partial}{\partial t}\left(\vec{\nabla}\times\mathbf{B}\right)$$

$$\vec{\nabla}\times\left(\vec{\nabla}\times\mathbf{E}\right)=\vec{\nabla}\left(\vec{\nabla}\bullet\mathbf{E}\right)-\nabla^2\mathbf{E}=-\nabla^2\mathbf{E}$$

Using: $\vec{\nabla}\cdot\mathbf{E}=0$

Maxwell's Equations to the wave equation

- Finish derivation of the wave equation

$$\vec{\nabla}\times\left(\vec{\nabla}\times\mathbf{E}\right)=-\nabla^2\mathbf{E}=-\frac{\partial}{\partial t}\left(\vec{\nabla}\times\mathbf{B}\right)$$

$$-\frac{\partial}{\partial t}\left(\vec{\nabla}\times\mathbf{B}\right)=-\frac{\partial}{\partial t}\left(\frac{1}{c^2}\frac{\partial\mathbf{E}}{\partial t}+\mu_0\frac{\partial\mathbf{P}}{\partial t}\right)=-\left(\frac{1}{c^2}\frac{\partial^2\mathbf{E}}{\partial t^2}+\mu_0\frac{\partial^2\mathbf{P}}{\partial t^2}\right)$$

$$\boxed{\nabla^2\mathbf{E}-\frac{1}{c^2}\frac{\partial^2\mathbf{E}}{\partial t^2}=\mu_0\frac{\partial^2\mathbf{P}}{\partial t^2}}$$

"Inhomogeneous Wave Equation"

- For a plane wave traveling in the z-direction,

$$\frac{\partial^2\mathbf{E}}{\partial z^2}-\frac{1}{c^2}\frac{\partial^2\mathbf{E}}{\partial t^2}=\mu_0\frac{\partial^2\mathbf{P}}{\partial t^2}$$

Other geometries dictate how to deal with the Laplacian operator

Linear WE, isotropic medium

- For linear response, the induced polarization is proportional to the incident field
  - If the medium is isotropic, then the susceptibility is a scalar

$$\mathbf{P}\left(\mathbf{E}\right)=\varepsilon_0\chi\mathbf{E},\quad \mathbf{D}=\varepsilon_0\mathbf{E}+\mathbf{P}=\varepsilon_0\left(1+\chi\right)\mathbf{E}=\varepsilon_0\varepsilon\,\mathbf{E}=\varepsilon_0 n^2\mathbf{E}$$

  - In this case, $\mathbf{P}\,||\,\mathbf{E},\quad \mathbf{D}\,||\,\mathbf{E}$

$$\frac{\partial^2\mathbf{E}}{\partial z^2}-\frac{1}{c^2}\frac{\partial^2\mathbf{E}}{\partial t^2}=\mu_0\frac{\partial^2\mathbf{P}}{\partial t^2}=\mu_0\varepsilon_0\chi\frac{\partial^2\mathbf{E}}{\partial t^2}=\frac{1}{c^2}\chi\frac{\partial^2\mathbf{E}}{\partial t^2}$$

$$\boxed{\frac{\partial^2\mathbf{E}}{\partial z^2}-\frac{n^2}{c^2}\frac{\partial^2\mathbf{E}}{\partial t^2}=0}$$

Using the fact that: $\varepsilon_0\mu_0=1/c^2$

Linear WE, anisotropic medium

- If the medium is anisotropic, the magnitude of the induced polarization is still proportional to the incident field
  - But now the susceptibility is a tensor

$$\mathbf{P}(\mathbf{E}) = \varepsilon_0 \vec{\vec{\chi}} \cdot \mathbf{E}, \quad \mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} = \varepsilon_0 \left(1 + \vec{\vec{\chi}}\right) \cdot \mathbf{E} = \varepsilon_0 \vec{\vec{\varepsilon}} \cdot \mathbf{E}$$

  - In this case, the medium re-orients the direction of the displacement vector
  - If the coordinate system is chosen to diagonalize the dielectric tensor,

$$\vec{\vec{\varepsilon}} = \begin{pmatrix} \varepsilon_{xx} & 0 & 0 \\ 0 & \varepsilon_{yy} & 0 \\ 0 & 0 & \varepsilon_{zz} \end{pmatrix} \quad \vec{\vec{\chi}} = \begin{pmatrix} \chi_{xx} & 0 & 0 \\ 0 & \chi_{yy} & 0 \\ 0 & 0 & \chi_{zz} \end{pmatrix}$$

Calculation of $\chi^{(1)}(\omega)$

- The polarization is just the density of individual dipole moments: $\mathbf{P} = N_a \mathbf{p} = -N_a e \mathbf{r} = N_a \alpha \mathbf{E}$ α = polarizability
- In 1D: $P = N_a p = -N_a e x$ Where x(t) is the position of the electron
- Method:
  - Assume one resonant frequency, ω_0 for the system
  - Assume one arbitrary input (driving) frequency, ω
  - Solve equation of motion for x(t):

$$m_e \ddot{x}(t) = -eE(t) - m_e \omega_0^2 x(t) - 2 m_e \gamma \dot{x}(t)$$

  - Calculate $\chi^{(1)}$:

$$P(t) = -N_a e x(t) = \varepsilon_0 \chi^{(1)} E(t) \rightarrow \chi^{(1)} = -\frac{N_a e x(t)}{\varepsilon_0 E(t)}$$

Solution for x(t)

- Equation of motion for x(t):

$$m_e\ddot{x}(t)+2m_e\gamma\dot{x}(t)+m_e\omega_0^2x(t)=-eE(t)=-eE_0e^{-i\omega t}+c.c.$$

  – Let $x(t)=x_0e^{-i\omega t}+c.c.$

$$-m_e\omega^2x_0e^{-i\omega t}-2i\omega\,m_e\gamma x_0e^{-i\omega t}+m_e\omega_0^2x_0e^{-i\omega t}+c.c.=-eE_0e^{-i\omega t}+c.c.$$

  – Collect terms with common time dependence into their own equation. This leads to separate (but identical) equations for exp(±*i ω t*) dependence:

$$-m_e\omega^2x_0-2i\omega\,m_e\gamma x_0+m_e\omega_0^2x_0=-eE_0$$

$$x_0(\omega)=-\frac{e}{m_e}E_0\frac{1}{\omega_0^2-2i\omega\gamma-\omega^2}\equiv-\frac{e}{m_e}E_0\frac{1}{D(\omega)}$$

"Resonant denominator"

Solution for $\chi^{(1)}(\omega)$ and $n(\omega)$

- Since $\chi^{(1)}=-\frac{N_a\,e\,x(t)}{\varepsilon_0E(t)}$

$$\chi^{(1)}=-\frac{N_a e}{\varepsilon_0}\left(-\frac{e}{m_e}E_0\frac{e^{-i\omega t}}{D(\omega)}\right)\frac{1}{E_0e^{-i\omega t}}=\frac{N_ae^2}{\varepsilon_0m_e}\frac{1}{D(\omega)}$$

- And

$$n^2=1+\chi^{(1)}=1+\frac{N_ae^2}{\varepsilon_0m_e}\frac{1}{D(\omega)}=1+\frac{N_ae^2}{\varepsilon_0m_e}\frac{1}{\omega_0^2-2i\omega\gamma-\omega^2}$$

- This assumes low density (e.g. gas). For solids/liquids, correct for local fields.
- Note that the index is complex: imaginary part leads to absorption (or possibly gain)

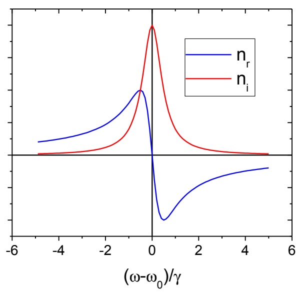
Complex refractive index

- Solve for real and imaginary parts

$$n \rightarrow n_r + in_i = 1 + \frac{N_a e^2(\omega_0^2 - \omega^2)}{2\varepsilon_0 m_e[(\omega_0^2 - \omega^2)^2 + \omega^2\gamma^2]} + i\frac{N_a e^2 \gamma\omega}{2\varepsilon_0 m_e[(\omega_0^2 - \omega^2)^2 + \omega^2\gamma^2]}$$

- Near the resonance,

$$n_r + in_i = 1 + \frac{N_a e^2(\omega_0 - \omega)}{4\varepsilon_0 m_e \omega_0[(\omega_0 - \omega)^2 + (\gamma/2)^2]} + i\frac{N_a e^2 \gamma}{8\varepsilon_0 m_e \omega_0[(\omega_0 - \omega)^2 + (\gamma/2)^2]}$$



Normalized plot of n-1 and k versus $w-w_0$

For more than one resonance,

$$n^2 = 1 + \frac{N_a e^2}{\varepsilon_0 m_e}\sum_j \frac{f_j}{(\omega_j^2 - \omega^2 - i\omega\gamma_j)}$$

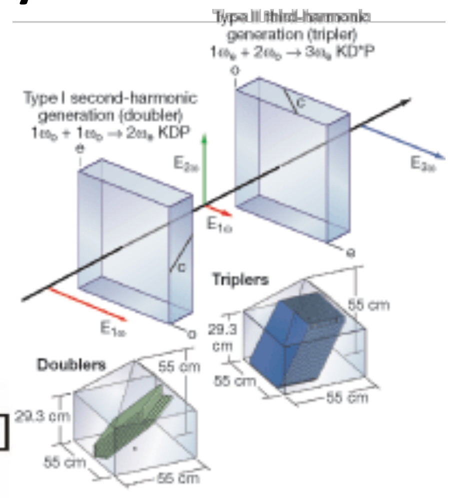
$\sum_j f_j = Z$ f = oscillator strength

Second harmonic generation

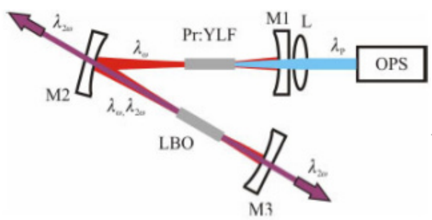
- Applications: frequency conversion IR to visible, visible to UV
  - External conversion
  - Intracavity conversion
- Nonlinear pulse characterization (autocorrelation)
- SHG requires asymmetric potential
  - Contrast mechanism in microscopy
  - Diagnostic of symmetry breaking in nanoparticles and molecules
  - Diagnostic of surface properties

Laser frequency conversion

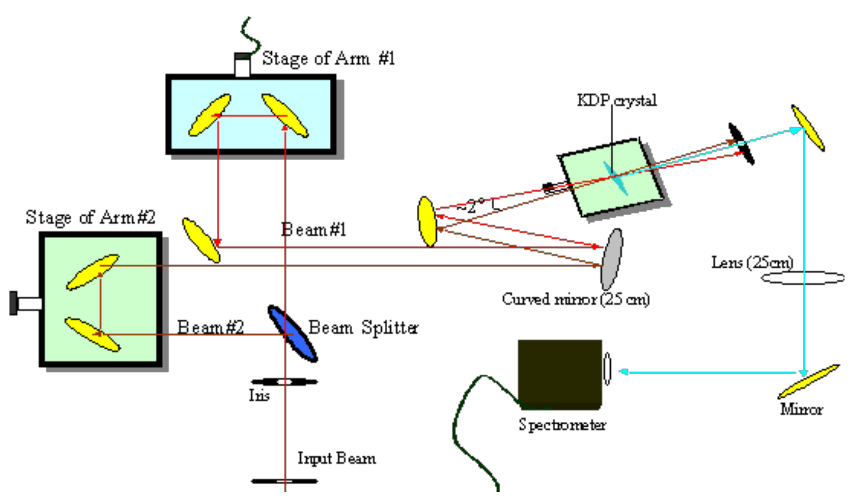
- External cavity



- Intracavity doubling

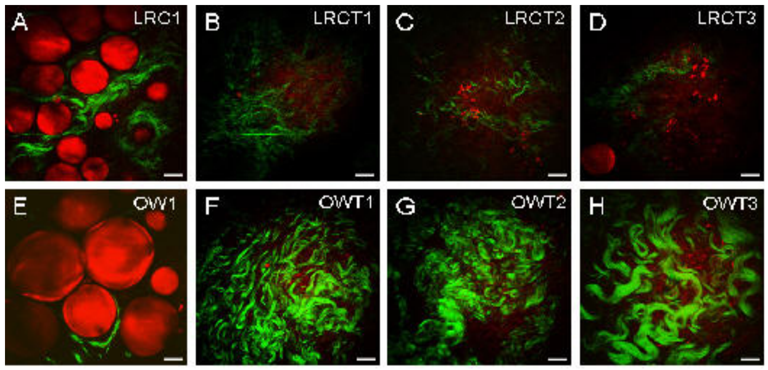


Application: Pulse characterization



Application: SHG microscopy

Red: CARS, coherent anti-stokes raman scattering
Green: SHG



Classical model for nonlinear response

- Extension of classical SHO model for dispersion
  - NL contribution to restoring force (derived from an anharmonic potential)
  - As before, we include resonant frequency, damping, driving oscillating field(s)
- Use a perturbative approach to solve for electron position, $x(t)=\lambda x^{(1)}(t)+\lambda^2 x^{(2)}(t)+\lambda^3 x^{(3)}(t)+\cdots$
  - Match orders of expansion parameter λ
  - Calculate orders of induced polarization.
- Can also numerically solve for response w/o approximation

Nonlinear wave equation

- Generalize for NL polarization

$$\nabla^2\mathbf{E}-\frac{1}{c^2}\frac{\partial^2\mathbf{E}}{\partial t^2}=\mu_0\frac{\partial^2\mathbf{P}}{\partial t^2}$$

 – For now, neglect vector character of response
 – Expand polarization as a Taylor series
  • Any 1/n! factors are included in definition of χ's

$$P=\varepsilon_0\left(\chi^{(1)}E+\chi^{(2)}E^2+\chi^{(3)}E^3+\cdots\right)$$

 – Separate linear from NL part: $P=\varepsilon_0\chi^{(1)}E+P^{NL}$
 – Now PNL is the source term to the linear eqn

$$\nabla^2 E-\frac{n^2}{c^2}\frac{\partial^2 E}{\partial t^2}=\mu_0\frac{\partial^2 P^{NL}}{\partial t^2}$$

Signal channels

- We've seen that the nonlinear polarization can have many frequency components (ω_n) and wave directions ($\mathbf{k}_n$)
- Total field is sum of all components:

$$\mathbf{E}(\mathbf{r},t)=\sum_{n>0}\mathbf{E}_n(\mathbf{r},t)=\sum_{n>0}\vec{\mathcal{E}}_n(\mathbf{r},t)\cos\left[\mathbf{k}_n\cdot\mathbf{r}-\omega_n t\right] \quad \textbf{Real field}$$

$$=\sum_{n>0}\left[\mathbf{A}_n(r,t)\exp\left(i\left(\mathbf{k}_n\cdot\mathbf{r}-\omega_n t\right)\right)+c.c.\right]$$

 – In general, there can be different k's at the same frequency ω_n (e.g. diffraction from NL grating)
 – With this convention, field envelopes are $\boxed{\mathbf{A}_n=\tfrac{1}{2}\vec{\mathcal{E}}_n}$

Intensity calculation

- Time average intensity can be calculated from the field:

$$I_n = \tfrac{1}{2}\varepsilon_0 nc\left|\overrightarrow{\mathcal{E}_n}\right|^2 = \tfrac{1}{2}\varepsilon_0 nc\overrightarrow{\mathcal{E}_n}\cdot\overrightarrow{\mathcal{E}_n}^*$$

- With the convention that $\boxed{\mathbf{A}_n = \tfrac{1}{2}\overrightarrow{\mathcal{E}_n}}$

$$I_n = 2\varepsilon_0 nc\left|\mathbf{A}_n\right|^2 = 2\varepsilon_0 nc\mathbf{A}_n\cdot\mathbf{A}_n^*$$

- Now we can write the field over a sum of ± frequencies

$$\mathbf{E}(\mathbf{r},t) = \sum_n\left[\mathbf{A}_n(r,t)\exp\left(i\left(\mathbf{k}_n\cdot\mathbf{r}-\omega_n t\right)\right)+c.c.\right]$$

Generalized NL polarization

$$\mathbf{P}(\mathbf{r},t) = \sum_n\left[\mathbf{P}_n(r,t)\exp\left(i\left(\mathbf{k}_n\cdot\mathbf{r}-\omega_n t\right)\right)+c.c.\right]$$

- NL polarization does not necessarily point in the same direction as E field: must use tensors
- Second-order example: cartesion $\{i,j,k\}\in\{1,2,3\}$

$$P_i(\omega_n+\omega_m) = \varepsilon_0\sum_{jk}\sum_{(nm)}\chi^{(2)}_{ijk}(\omega_n+\omega_m;\omega_n,\omega_m)E_j(\omega_n)E_k(\omega_m)$$

  - Output i'th polarization direction, frequency $\omega_n+\omega_m$
  - Input polarization directions j, k, frequenies ω_n, ω_m
  - Sum (n m) so that $\omega_n+\omega_m$ is constant
  - Sum over + and – frequencies!

2^{nd} order NL polarization example

- The susceptibility is a *tensor* **P** is in a different direction from **E**, each component of $\chi_{ijk}^{(2)}$ is a function
- Consider sum mixing to produce $\omega_3=\omega_1+\omega_2$ along the x-direction. The x component of the NL polarization is

$$P_1(\omega_3)=\varepsilon_0\sum_{jk}\begin{bmatrix}\chi_{1jk}^{(2)}(\omega_3;\omega_1,\omega_2)E_j(\omega_1)E_k(\omega_2)+\\ \chi_{1jk}^{(2)}(\omega_3;\omega_2,\omega_1)E_j(\omega_2)E_k(\omega_1)\end{bmatrix}$$

  - Permuting input frequencies
  - For a given set of input, output freq, $\chi_{1jk}^{(2)}$ is a 3x3 matrix

2^{nd} order NL polarization example

- All this looks hopelessly complicated, but typically…
  - We specify input frequencies and polarization
  - Phase matching allows us to focus on one output combination
  - Away from resonances, χ components indep of ω
- Examples: input $E_y(\omega_1)$ and $E_x(\omega_2)$

$$P_1(\omega_3)=\varepsilon_0\left[\chi_{121}^{(2)}E_2(\omega_1)E_1(\omega_2)+\chi_{112}^{(2)}E_1(\omega_2)E_2(\omega_1)\right]$$

- Input along y-direction $E_y(\omega_1)$ and $E_y(\omega_2)$

$$P_1(\omega_3)=2\varepsilon_0\chi_{122}^{(2)}E_2(\omega_1)E_2(\omega_2)$$

- Because of crystal symmetry, many tensor components are either 0 or identical to others
- Negative frequency components go with conjugated fields