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

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

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

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

Using the fact that:

$$\varepsilon_0 \mu_0 = 1/c^2$$

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

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

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

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

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

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):

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

  - 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 $\chi^{(1)} = -\dfrac{N_a e\, x(t)}{\varepsilon_0 E(t)}$

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

- And

$$n^2 = 1+\chi^{(1)} = 1+\frac{N_a e^2}{\varepsilon_0 m_e}\frac{1}{D(\omega)} = 1+\frac{N_a e^2}{\varepsilon_0 m_e}\frac{1}{\omega_0^2 - 2i\omega\gamma - \omega^2}$$

- 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)

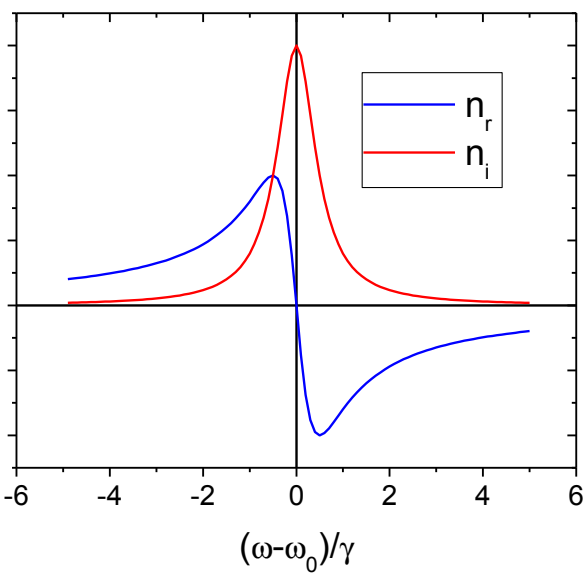
Complex refractive index

- Solve for real and imaginary parts

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

- 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,

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

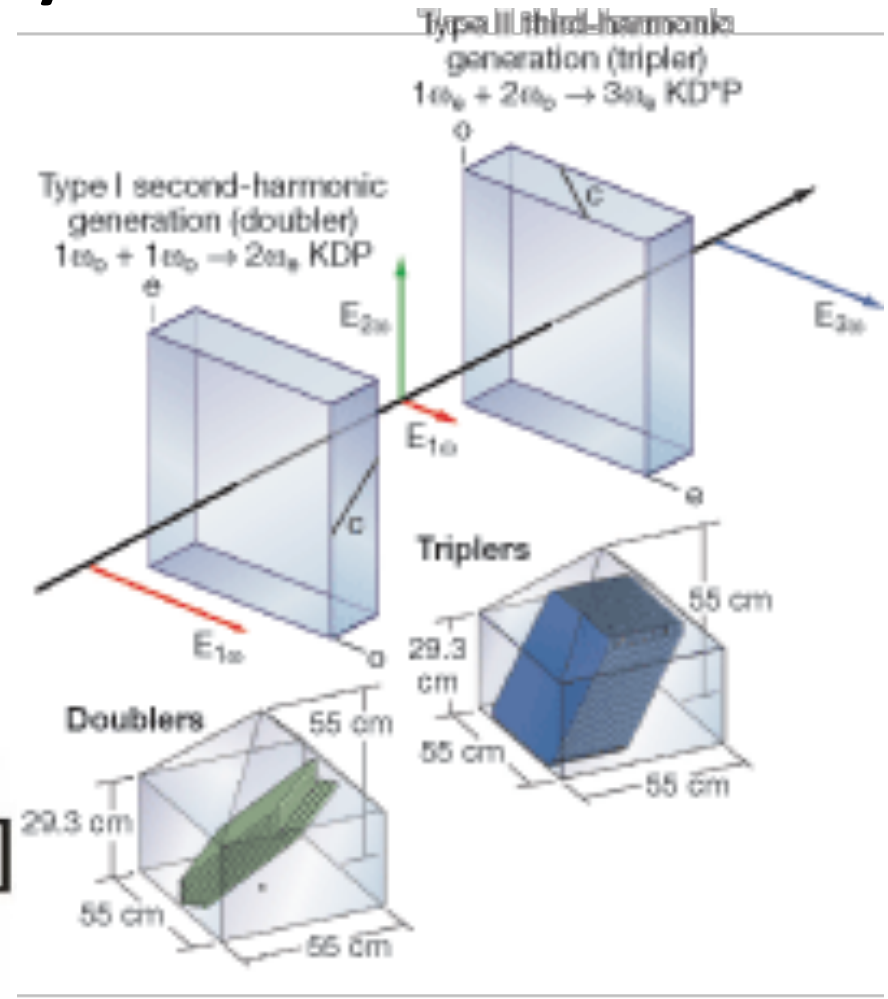
$\sum_j f_j = Z$ f = oscillator strength

Second harmonic generation

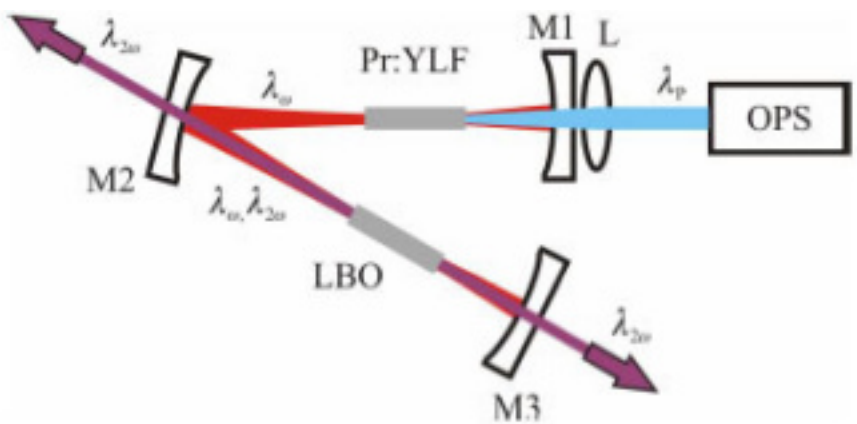
- Applications: frequency conversion IR to visible, visible to UV
  - External conversion
  - Intracavity conversion
- Nonlinear pulse characterization (autocorrelation)
- SHG requires asymmetric potential
  - Contrast mechanism in microscopy
  - Diagnostic of symmetry breaking in nanoparticles and molecules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

Laser frequency conversion

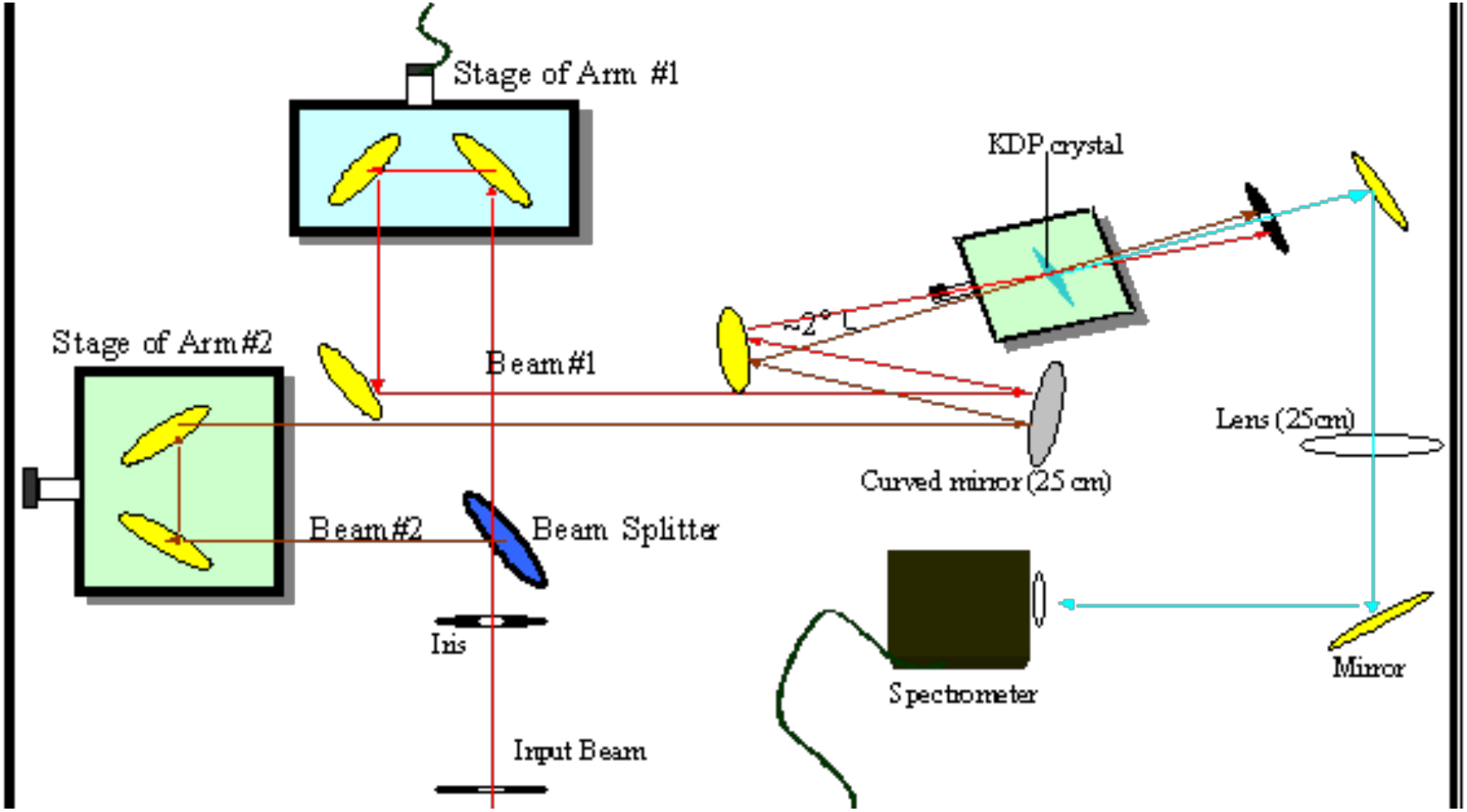
- External cavity



- Intracavity doubling



Pulse characterization



SHG microscopy

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