Optical methods in chemistry
or
Photon tools for chemical sciences

Session 10:

Course layout – contents overview and general structure

- Introduction and ray optics
- Wave optics
- Beams
- From cavities to lasers
- More lasers and optical tweezers
- From diffraction and Fourier optics
- Microscopy
- Spectroscopy
- Electromagnetic optics
- **Absorption, dispersion, and non-linear optics**
- Ultrafast lasers
- Introduction to x-rays
- X-ray diffraction and spectroscopy
- Summary

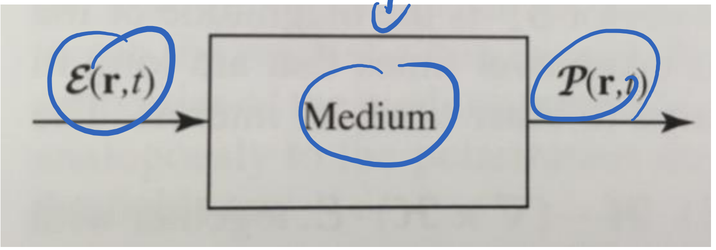
Today:

More materials properties, linear and non-linear

Electromagnetic waves in dielectric media

interpretation: output response

General



in response to an electrical field $\mathcal{E}$ medium creates a polarization

instantaneous   no r   no direction

But stick with linear, nondispersive, homogenous, and isotropic media right now: $\mathcal{E} \rightarrow \boxed{M} \rightarrow P$

Simplifying

$$\mathcal{P} = \epsilon_o \chi \mathcal{E},$$

$\rightarrow$ electric susceptibility

$\rightarrow \varepsilon = \varepsilon_0 (1 + \chi)$

$\uparrow$ dielectric constant

χ scalar

$\mathcal{E} \rightarrow \boxed{\chi} \rightarrow P$

$D = \varepsilon \mathcal{E} \quad | \quad \varepsilon = \varepsilon_0 (1 + \chi)$

This leads to the following Maxwell and wave equations wave equations

$$\nabla \times \mathcal{H} = \epsilon \frac{\partial \mathcal{E}}{\partial t}$$

$$\nabla \times \mathcal{E} = -\mu \frac{\partial \mathcal{H}}{\partial t}$$

$$\nabla \cdot \mathcal{E} = 0$$

$$\nabla \cdot \mathcal{H} = 0.$$

ε — dielectric constant

μ — magnetic permeability

back to wave equation

$$\left.\nabla^2 u - \frac{1}{c^2}\frac{\partial^2 u}{\partial t^2} = 0 \right\} \text{ in media}$$

$$c = \frac{1}{\sqrt{\varepsilon\mu}}$$

define $n = \frac{c_0}{c} = \sqrt{\frac{\varepsilon}{\varepsilon_0} \cdot \frac{\mu}{\mu_0}}$ = refraction index

non-magnetic materials

$$n = \sqrt{\frac{\varepsilon}{\varepsilon_0}} = \sqrt{1 + \chi}$$

Homework

familiarize yourself with this kind of e-dynamics

Generalized optical constant

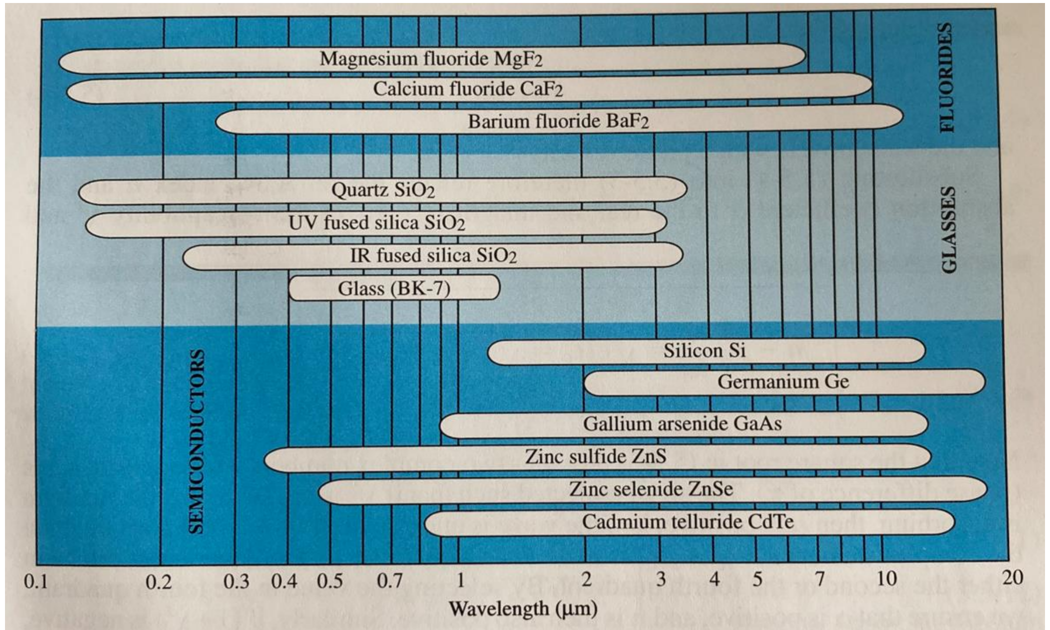


Figure 5.5-1 Spectral bands within which selected optical materials transmit light.

So far - assumed media to be transparent

- linear interactions

↳ But we know there is absorption!

Phenomenological Approach: add 2nd component to the refractive index
independent variable → complex number

from $n \sim \sqrt{1+\chi}$
↳ $\chi = \chi' + i\chi''$

note that $\varepsilon = \varepsilon_0(1+\chi)$ (permittivity)
and all others will also become complex

Absorption: The imaginary part

Helmholtz equation $\nabla^2 u + k^2 u = 0$ with complex u

but we also have $k = \omega\sqrt{\varepsilon\mu} = k_0\sqrt{1+\chi} = k_0\sqrt{1+\chi'+i\chi''}$

define k as complex and separate

$$k = \beta - i\tfrac{1}{2}\alpha = k_0\sqrt{1+\chi'+i\chi''}$$

in wave equation

look at α:
$(-ikz) \ldots (-(-i^2 k\alpha)$

$$A\exp(-ikz)$$

$$A\exp(-\tfrac{1}{2}\alpha z)\exp(-i\beta z)$$

$\Rightarrow$ Envelope A attenuated by $\exp(-\frac{1}{2}\alpha z)$

$\Rightarrow$ absorption $\alpha > 0$ absorption coefficient

Complex refractive index

General:

$$\boxed{n - j\frac{1}{2}\frac{\alpha}{k_o} = \sqrt{\epsilon/\epsilon_o} = \sqrt{1+\chi' + j\chi''}.}$$

Relationship between n, α, and χ

Weakly absorbing media: (glass in optical regime)

$$\boxed{\begin{aligned} n &\approx \sqrt{1+\chi'} \\ \alpha &\approx -\frac{k_o}{n}\chi''. \end{aligned}}$$

Refractive index is determined by $n = \sqrt{1+\chi'}$

α is small (no absorption)

$n \sim \chi'$

Dispersion: The real part

$\longrightarrow$ fct of ν

Remember $\mathcal{E} \rightarrow \boxed{\text{Mat}} \rightarrow P$

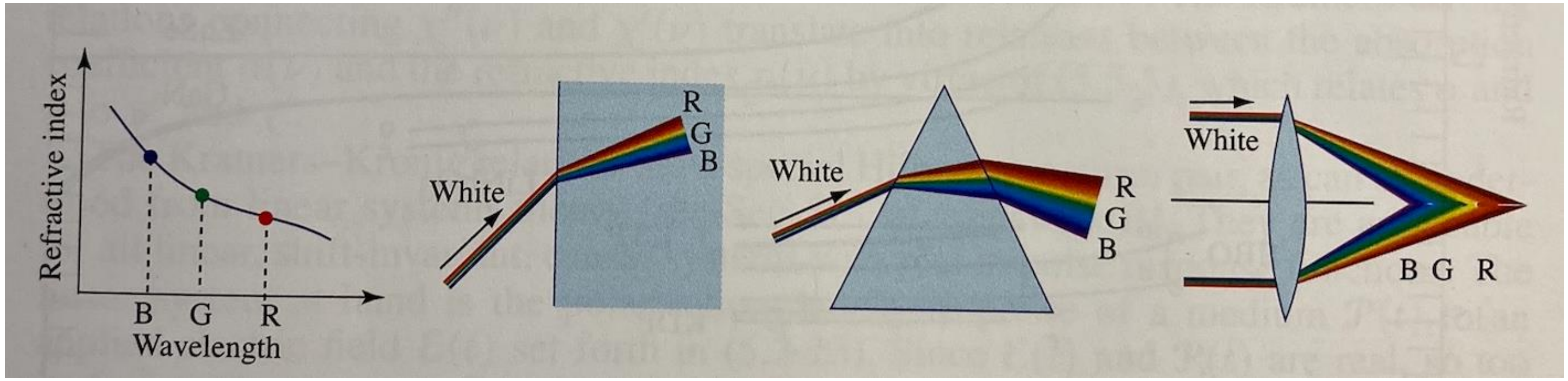
$P = \varepsilon_0 \chi \mathcal{E}$

$\Updownarrow$

now frequency dependent

Refractive index fct of ν

$f(\nu)$



$$A = \underbrace{A \exp\left(-\tfrac{1}{2}\alpha z\right)}_{\text{absorption}} \underbrace{\exp(-i\beta z)}_{\text{wave propagation}}$$

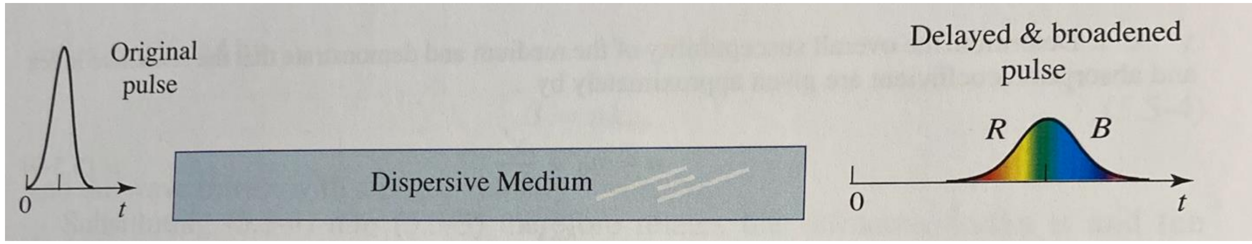
Relationship $k = \beta - i\tfrac{1}{2}\alpha = k_0\sqrt{1+\chi' + i\chi''}$

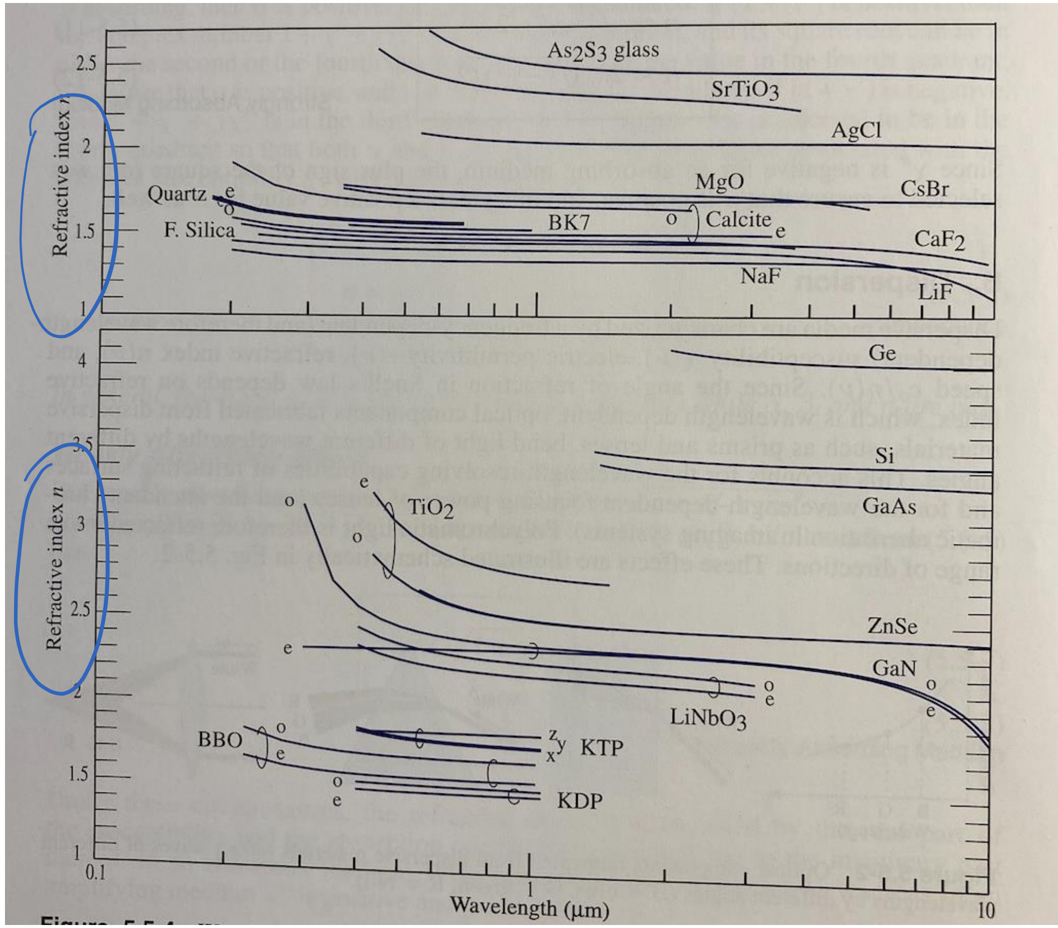
Now $\chi \rightarrow \chi(\nu) \rightarrow$ frequency dependent

$\rightarrow$ everything is frequency dependent

$$A = \;\ldots\ldots\; \exp(-i\beta(\nu) z)$$ is fct of ν

A short pulse in a dispersive medium





pulse propagation → velocities

→ fct of $\chi'(\nu)$

→ diff't colors travel at diff't speeds

→ arrive at diff't times

→ broadened

wavelength / frequency

↳ refractive index fct of ν/λ

The Kramers-Kronig Relation

$$\chi'(\nu) = \frac{2}{\pi}\int_0^{\infty} \frac{s\chi''(s)}{s^2-\nu^2}\,ds$$

$$\chi''(\nu) = \frac{2}{\pi}\int_0^{\infty} \frac{\nu\chi'(s)}{\nu^2-s^2}\,ds.$$

Without too much maths

Absorption & dispersion are intimately related

$\Downarrow$

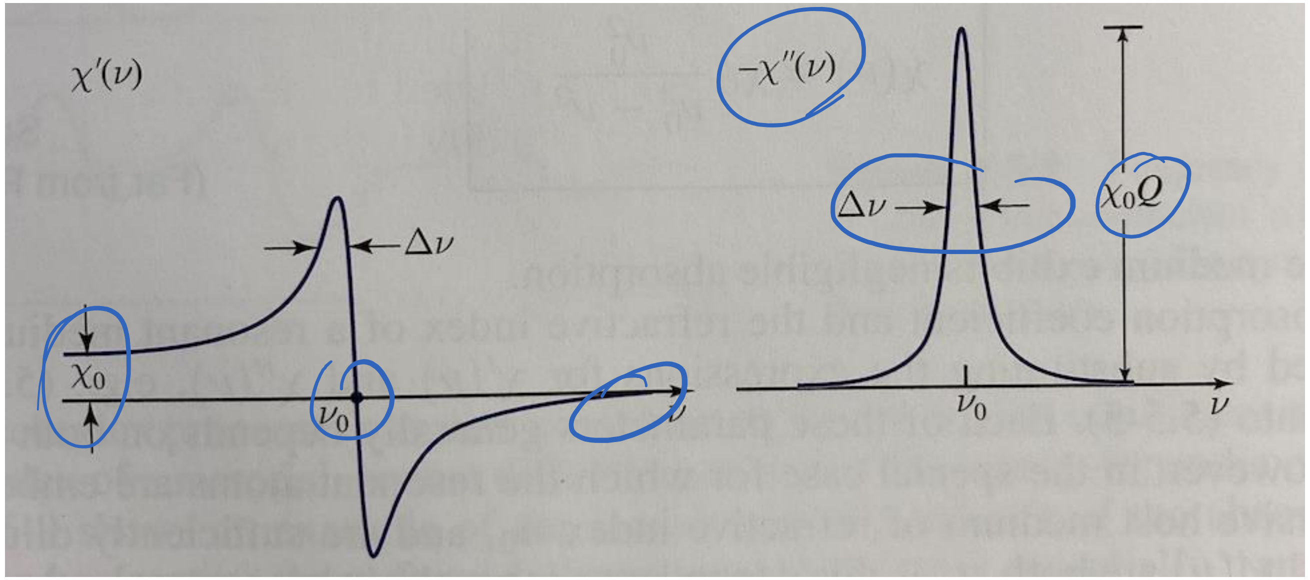
A dispersive material is also absorptive & vice versa

→ when you measure one property over a sufficient range you can determine the other one

→ Relates χ' and χ''

and therefore $\alpha, \beta, n, \ldots$

Resonances and refractive index



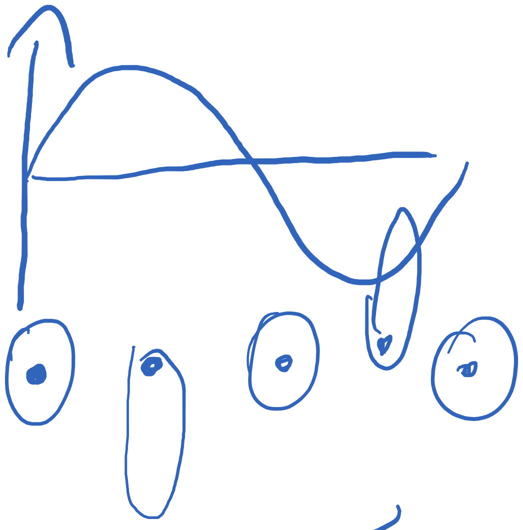
0-crossing at ν_0

absorption resonance

Remember

$$\frac{d^2x}{dt^2} + \sigma\frac{dx}{dt} + \omega_0 x = \frac{F}{m}$$

Note



Lorentz oscillator model

$$\frac{d^2P}{dt^2} + \sigma\frac{dP}{dt} + \omega_0^2 P = \omega_0^2 \varepsilon \chi E$$

Low frequency

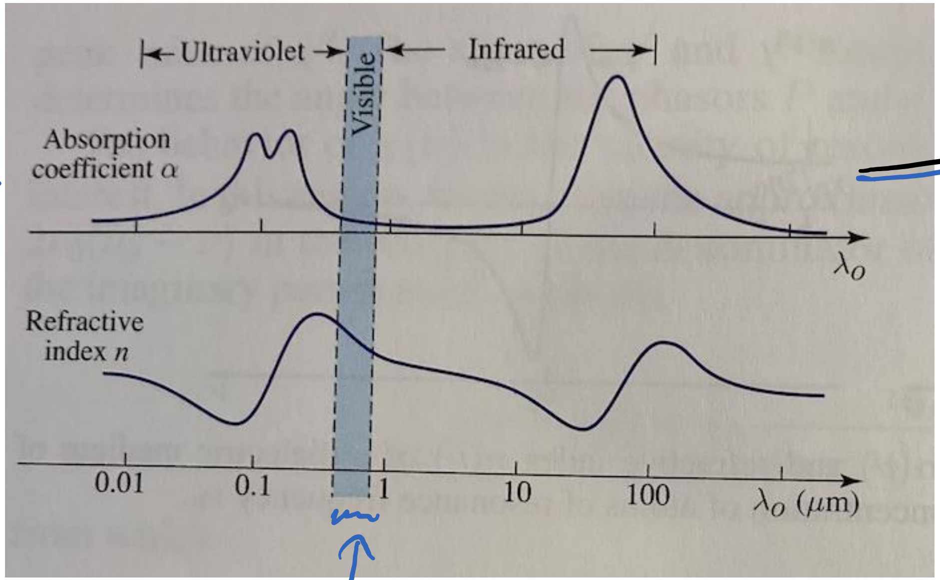
$\chi \sim \chi_0$

$\chi'' \to$ wave in medium (weak absorption)

above resonances $\chi' \to 0$ $\chi'' \to 0$ $\Rightarrow$ "free space"

A real optical (transparent) material

x-rays
Core electrons



lower frequencies

your experience

⇒ bottom line: a material is never really fully transparent

↳ "easy" refractive index works only in selected regimes

From linear to non-linear

Back to formal description of light as EM wave (from Session 9)

in vacuum

$$\nabla \times \mathcal{H} = \epsilon_o \frac{\partial \mathcal{E}}{\partial t}$$
$$\nabla \times \mathcal{E} = -\mu_o \frac{\partial \mathcal{H}}{\partial t}$$
$$\nabla \cdot \mathcal{E} = 0$$
$$\nabla \cdot \mathcal{H} = 0,$$

dielectric, homogeneous

$$\mathcal{E}(\mathbf{r},t) \longrightarrow \boxed{\text{Medium}} \longrightarrow \mathcal{P}(\mathbf{r},t)$$

But stick with linear, nondispersive, homogenous, and isotropic media right now:

$$\mathcal{P} = \epsilon_o \chi \mathcal{E},$$

Polarization density

Σ dipole moments induced by ext. electric field

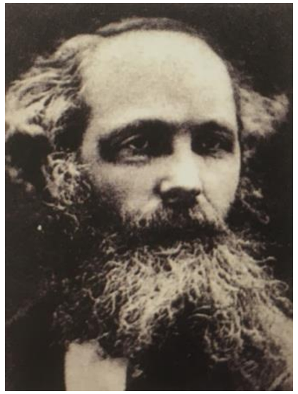
$$\mathcal{E} \rightarrow \boxed{\chi} \rightarrow \mathcal{P}$$

in dielectric media

$$\nabla \times \mathcal{H} = \epsilon \frac{\partial \mathcal{E}}{\partial t}$$
$$\nabla \times \mathcal{E} = -\mu \frac{\partial \mathcal{H}}{\partial t}$$
$$\nabla \cdot \mathcal{E} = 0$$
$$\nabla \cdot \mathcal{H} = 0.$$

$$\nabla^2 u - \frac{1}{c^2}\frac{\partial^2 u}{\partial t^2} = 0$$

$$\rightarrow n = \frac{c}{c_o} = \sqrt{\frac{\varepsilon}{\varepsilon_o}\frac{\mu}{\mu_o}}$$



James Maxwell
1831 - 1879

Generalization of susceptibility χ (still linear)

- Inhomogenous media $\chi \rightarrow \chi(r)$ fct of r
- Anisotrope media $\chi \rightarrow \chi(ij)$ tensor
- Dispersive media $\chi \rightarrow \chi(t)$ time dependent

General:

$$E(r,t) \rightarrow \boxed{\chi(r,t)} \rightarrow P(r,t)$$

Interpretation: Dynamic relationship between E an P

- E induces bound electrons in material to oscillate
- Time-dependent Polarization density P(t)
- Time-delay between E(t) and P(t)

Classically describe as harmonic oscillators

→ light induced distortion

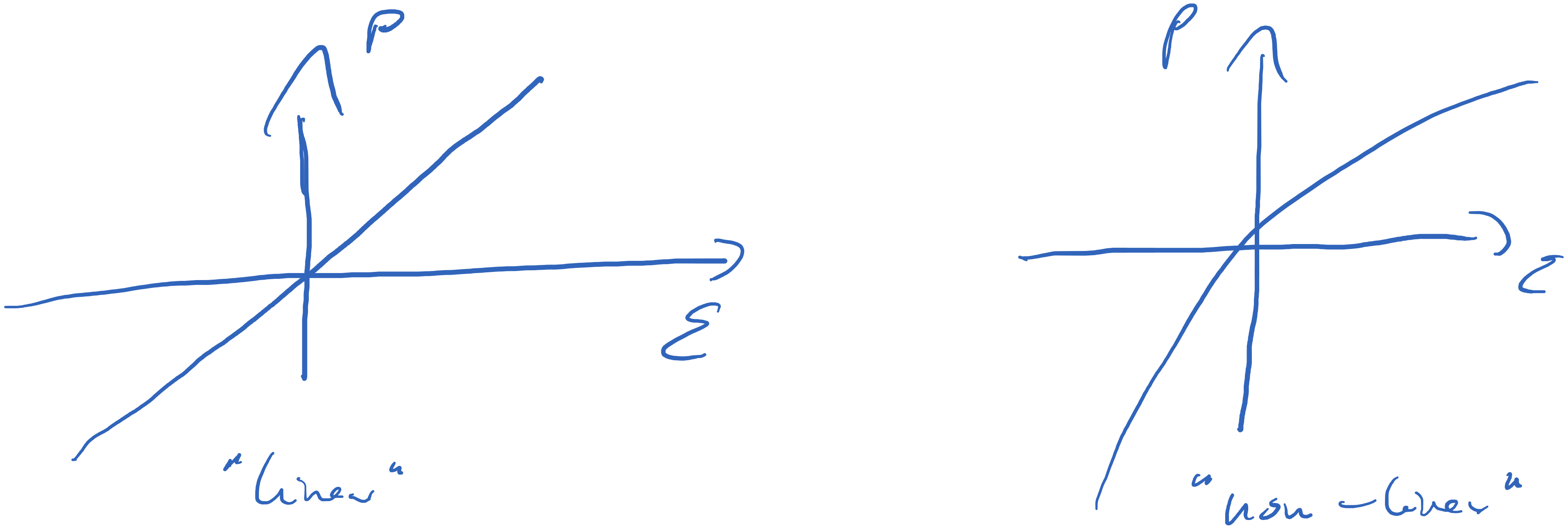
⇓

Lorentz oscillator model

Non-linear optical media

Handwaving:

- Linear: restoring force of light induced fields linear (“Hookes law applies”)
- Non-linear: Light induced fields comparable to inter-atomic fields in crystal (”no more linear forces”)
- (Note: fields still weak compared to intra-atomic fields – that is a later topic)



$\boxed{\Rightarrow \text{optical response can change in intense fields}}$

Expanded description of relationship between Polarization density P and Electric field E

Generally $\quad P = \varepsilon_0 \chi E \qquad \chi \rightarrow$ details unknown

Solution $\quad$ Taylor expansion

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

linear $\quad$ 2nd order non-linearity $\quad$ 3rd order non-linearity

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Sometimes written as

$$P = \varepsilon_0 \chi E + 2 d E^2 + 4 \chi^3 E^3 + \ldots$$

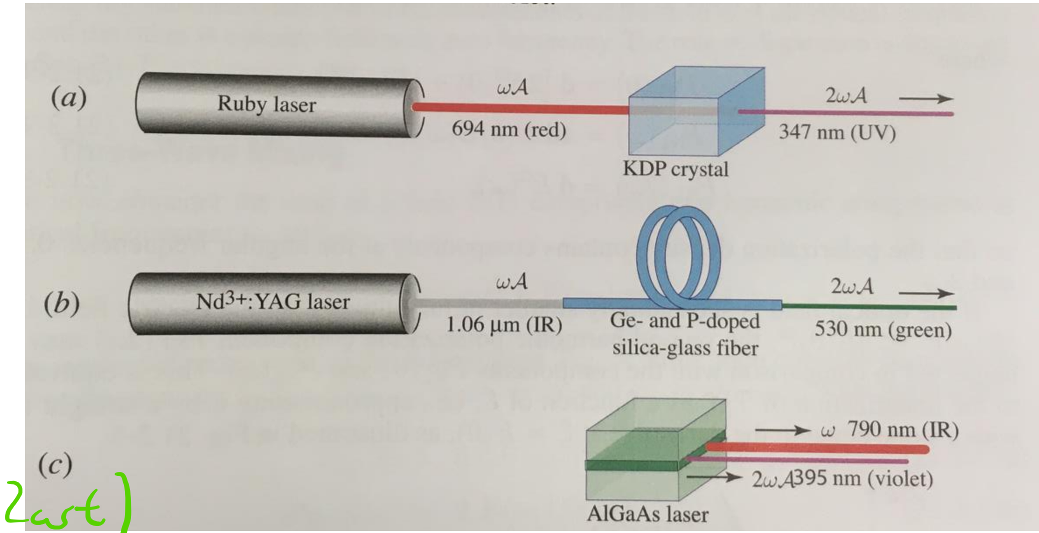
Second order non-linear optics example: Second harmonic generation

$$P = \varepsilon_0 \chi \mathcal{E}$$

$$P = \varepsilon_0 \left(\chi \mathcal{E} + \chi_2 \mathcal{E}^2 + \dots\right)$$

$$\mathcal{E} = \mathcal{E}_0 \sin \omega t$$

$$P = \varepsilon_0 \chi \mathcal{E}_0 \sin \omega t + \varepsilon_0 \chi^2 \mathcal{E}_0^2 \sin^2 \omega t + \dots$$



use: $\sin^2 \omega t = \frac{1}{2}(1 - \cos 2\omega t)$

$$= \text{linear term} + \frac{\varepsilon_0 \chi_2}{2} \mathcal{E}_0^2 (1 - \cos 2\omega t) + \dots$$

use "non-linear" crystals

(three wave mixing)

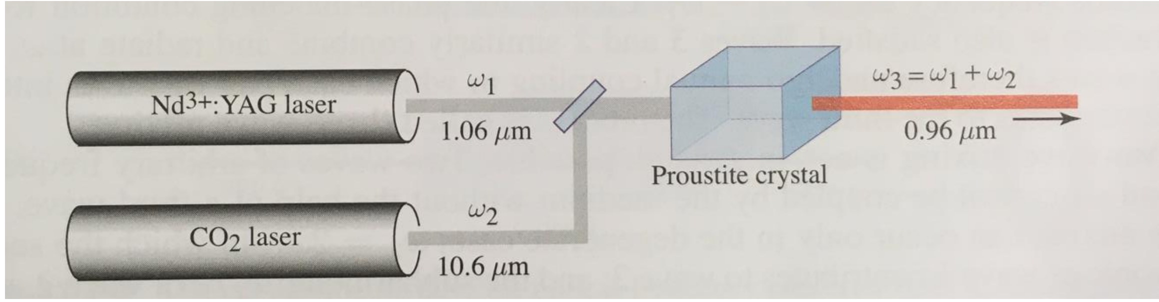
Second order non-linear optics example: Sum frequency generation

$\mathcal{E} = \mathcal{E}_{01} \sin\omega_1 t + \mathcal{E}_{02} \sin\omega_2 t$

$\Rightarrow$ squared term

$\sim \varepsilon_0 \chi_2 (\mathcal{E}_{01}^2 \sin^2\omega_1 t + \mathcal{E}_{02}^2 \sin^2\omega_2 t + 2\mathcal{E}_{01}\mathcal{E}_{02} \sin\omega_1 t \sin\omega_2 t$

$\rightsquigarrow$ component $\sim \omega_1 \pm \omega_2$



Second order non-linear crystal can allow mix two optical waves

$\Rightarrow$ frequency up/down conversion

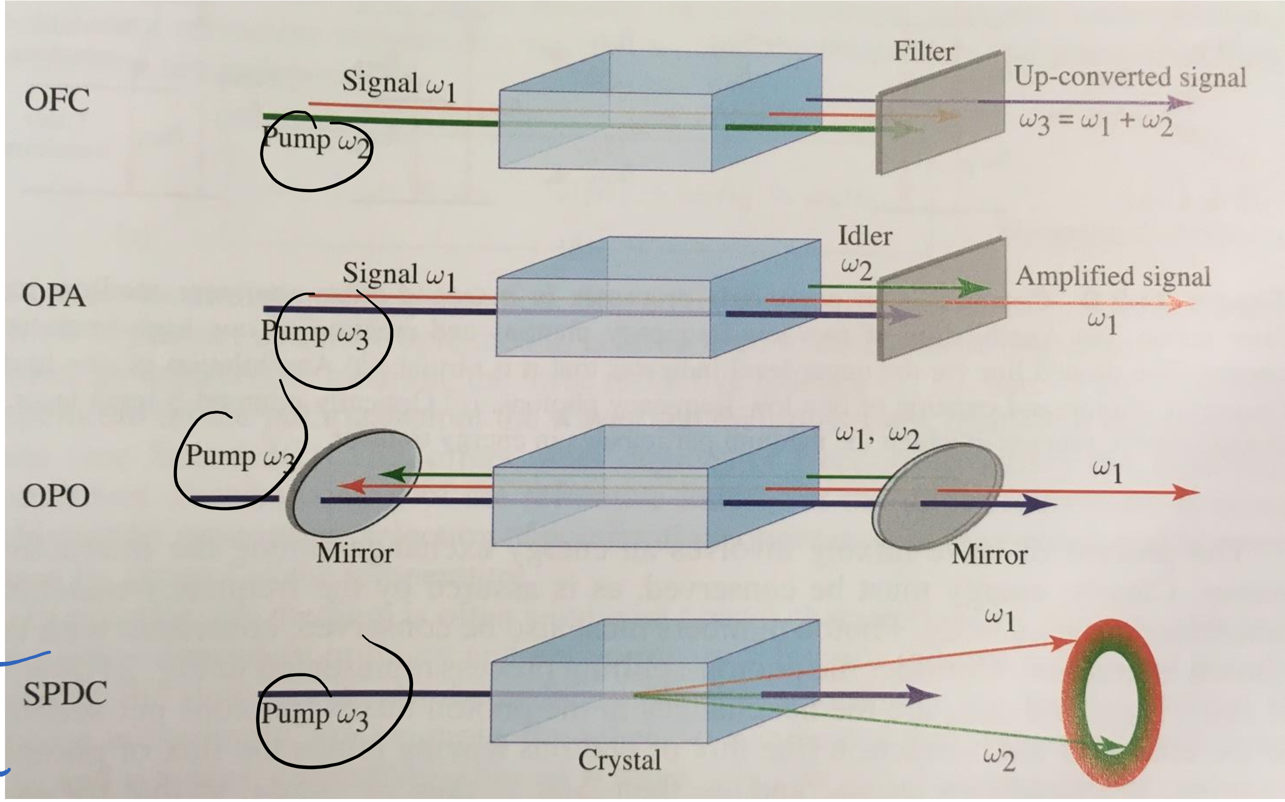
Second order non-linear optics example: Optical parametric devices

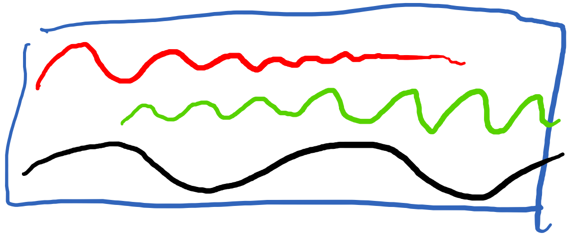
Optical frequency conversion

Optical parametric amplifier

Optical parametric oscillator

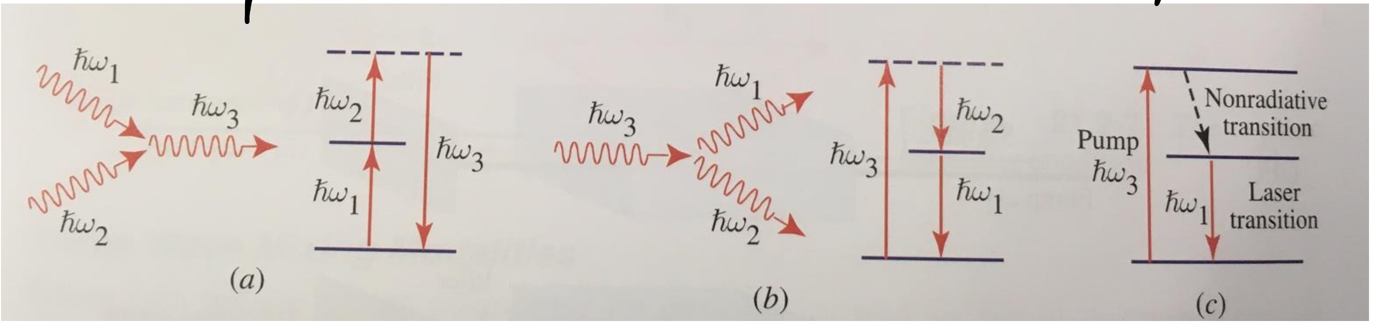
Spontaneous conversion





Second order non-linear optics example: Description as photon interaction process

up   down   parametric process



always

momentum + energy conservation

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

$\hbar\vec{k}_1 + \hbar\vec{k}_2 = \hbar\vec{k}_3$

(medium participates in energy transfer)

Third order non-linear optics example: Third-harmonic generation

↳ in principle same process with next term

could also generate 3ω light

but conversion efficiency low

$\Downarrow$

if you want higher order light

→ better approach of 2^{nd} harmonic + frequency mixing

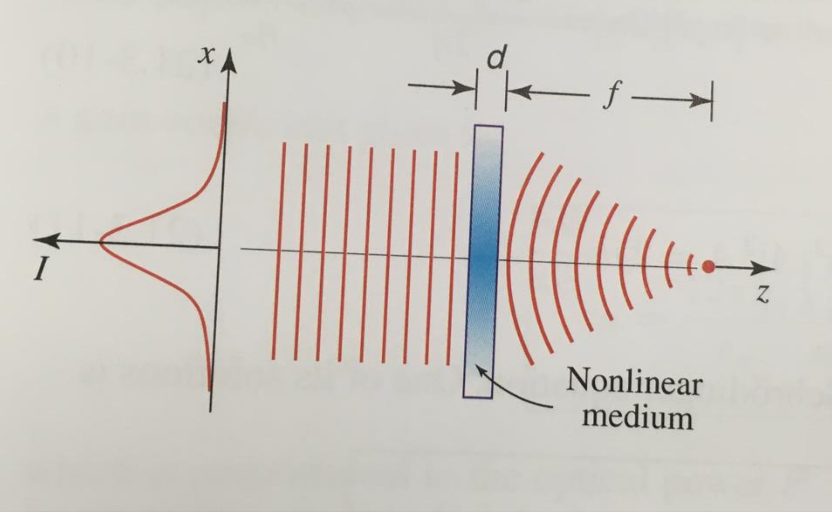
2x 2^{nd} process is more efficient

Third order non-linear optics example: Optical Kerr Effect and Self-Focusing

You can show that in 3rd order non-linearity you can

$\boxed{\text{intensity dependent refractive index}}$

$$n(I) = n + n_3 I$$

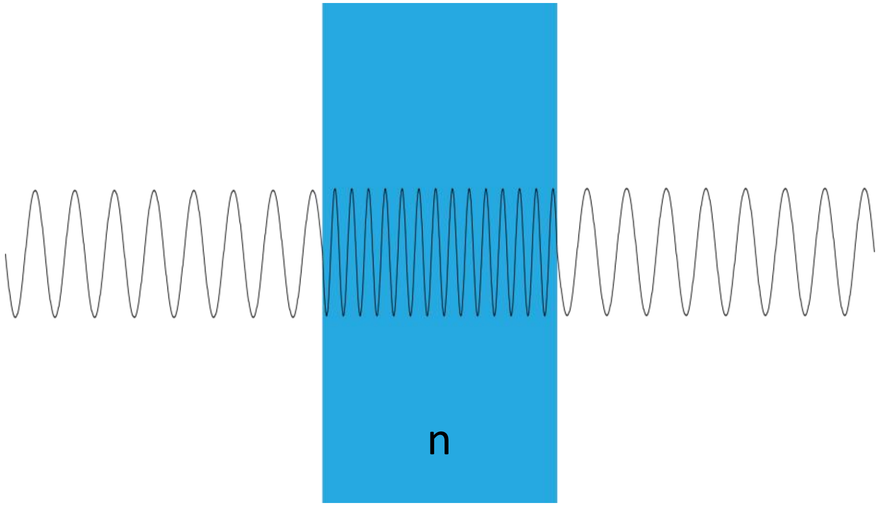


⇒ you can use light (pulse) to change optical properties itself

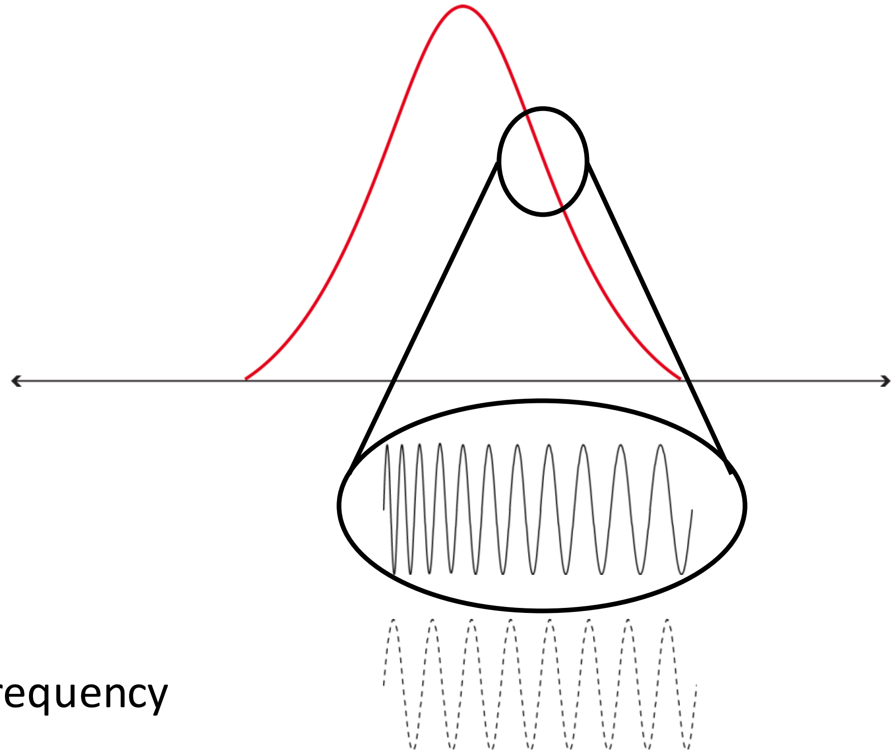
⇒ Gaussian beam → intensity dependent lens

Third order non-linear optics example: Self-phase modulation

normal refractive index



time-dependent refractive index



$$\omega(t) = -\frac{d\varphi(t)}{dt}$$; instantaneous frequency

- Conceptually – consider a plane monochromatic wave
- Time-dependent index leads to time-dependent frequency
- New frequency components are generated

The end.