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

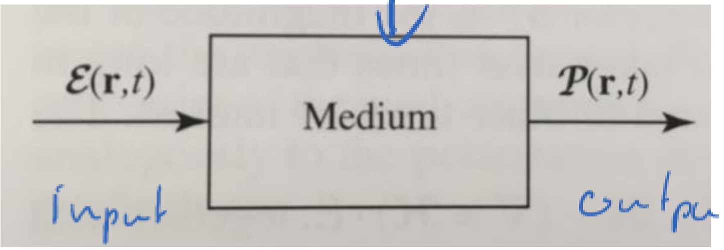
Today:

More materials properties, linear and non-linear

Electromagnetic waves in dielectric media

interpretation → output response

General



in response to an electric field $\mathcal{E}$
media creates a polarization

"instantaneous" "no $\vec{r}$" "no direction"

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

simplify to

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

→ electric susceptibility

χ scalar

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

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

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

dielectric constant
" electric permittivity

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 (electric permittivity)

μ – magnetic permeability

back to wave equation

$$\nabla^2 u - \frac{1}{c^2}\frac{\partial^2 u}{\partial t^2} = 0 \quad \Big| \text{ in medium}$$

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

define $n = c_0/c = \sqrt{\frac{\varepsilon}{\varepsilon_0}\frac{\mu}{\mu_0}}$ = refractive index!

non-magnetic materials

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

Generalized optical constant

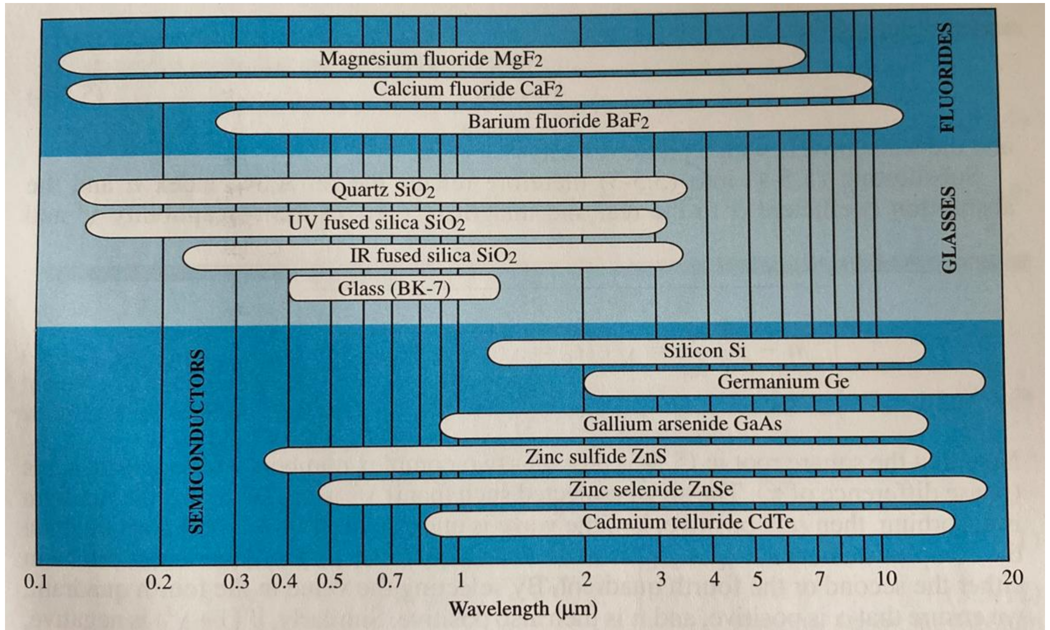


Figure 5.5-1 Spectral bands within which selected optical materials transmit light.

So far:

- assumed media to be transparent
- linear interactions

But we know:

- there is absorption

(Phenomenological) Approach:

→ add a second component to refractive index

independent variable → complex number

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

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

now also k complex: $k = \omega\sqrt{\varepsilon\mu_0} = k_0\sqrt{1+\chi} = k_0\sqrt{1+\chi'+i\chi''}$

define k as complex and separate variables

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

put back into wave equation

$$A\exp(-ikz)$$

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

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

$\Rightarrow$ absorption $\quad \alpha > 0$ – 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)

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

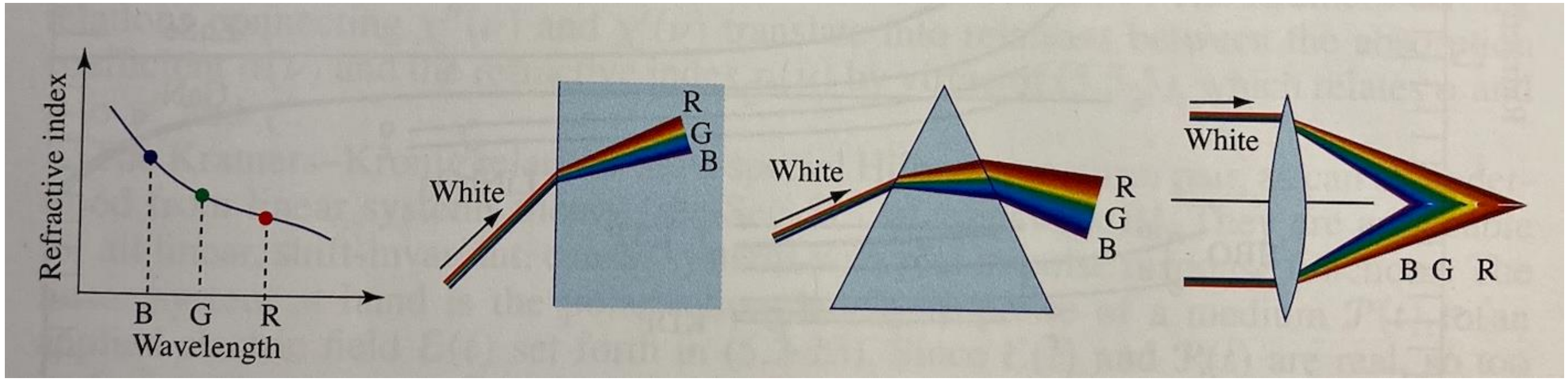
Refractive index determined by $n = \sqrt{1+\chi'}$

α small (no absorption)

$n \sim \chi'$

Dispersion: The real part $\longrightarrow$ fct of ν (frequency)

Refractive index $n(\nu)$



Remember

$\mathcal{E} \rightarrow \boxed{\text{Med}} \rightarrow P$

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

$\uparrow$

now ν-dependent

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

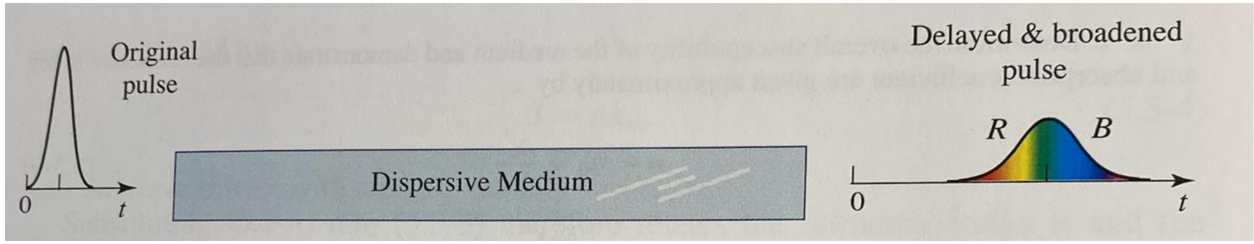
Relationship $\gamma = \beta - i\tfrac{1}{2}\alpha = k_0 \sqrt{1 + \chi' + \chi''}$

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

$\rightarrow$ everything is frequency dependent

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

A short pulse in a dispersive medium



↓

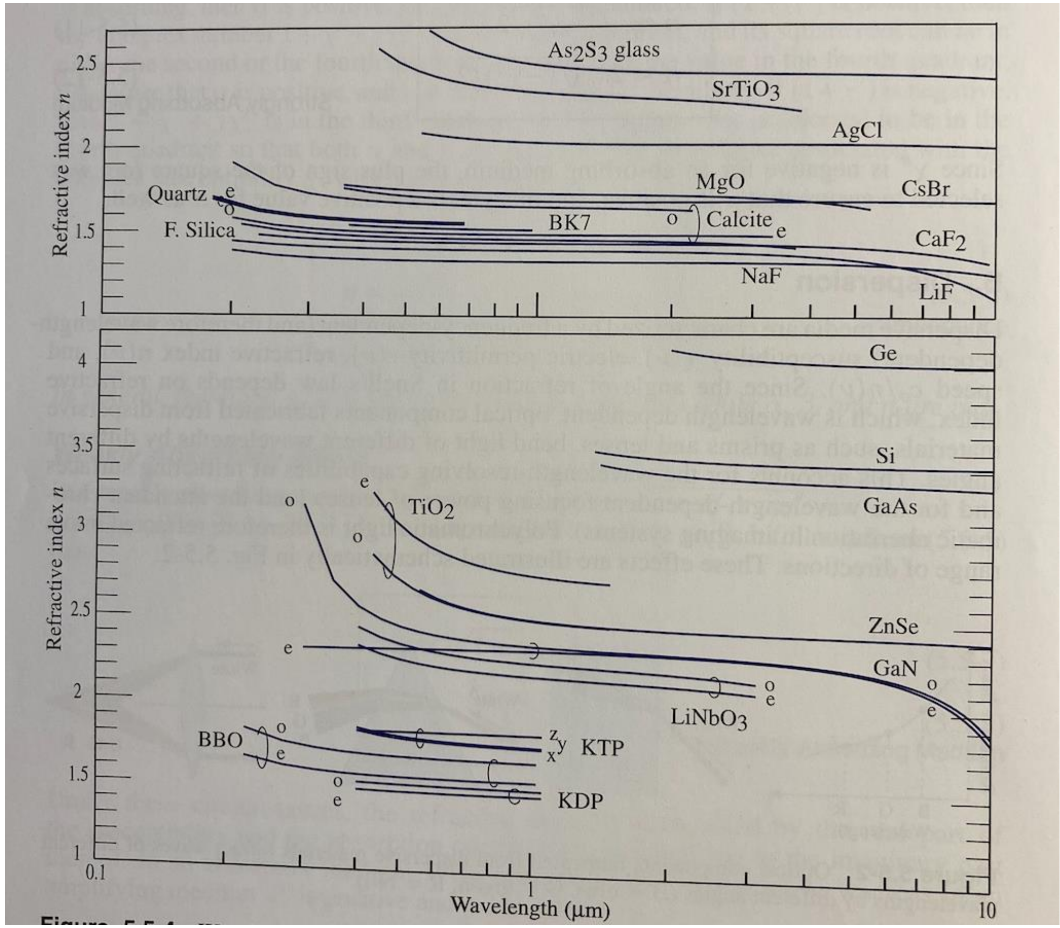
pulse propagation ⟷ velocities

→ fct of $\chi'(\nu)$

→ different colors travel at different speeds

→ arrive at different times

→ broadened



↳ wavelength / frequencies

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

$\Rightarrow$ if you measure one property of the refractive index over a significant range, you can determine the other one

$\rightarrow$ Relates χ' and χ'' and therefore $\alpha, \beta, n, \dots$

Resonances and refractive index

Treat in Lorentz oscillator model

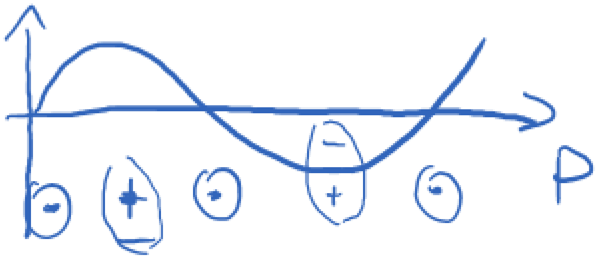
→ Again relate macroscopic to microscopic behavior

→ Remember oscillator

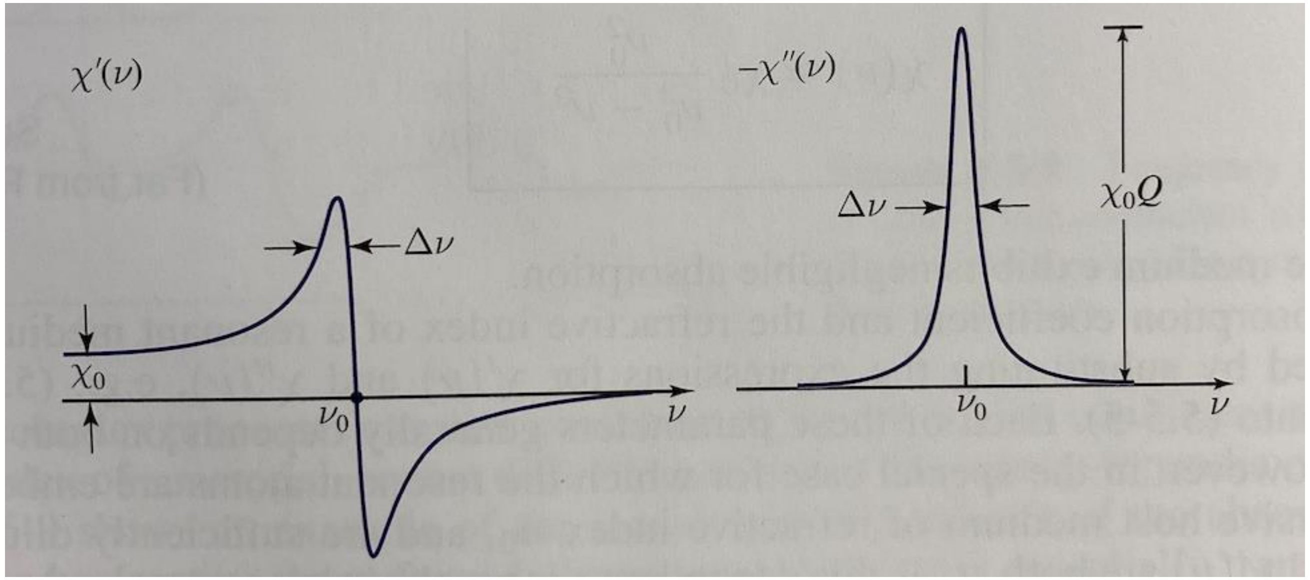
$$\frac{d^2x}{dt^2} + \sigma \frac{dx}{dt} + \omega_0^2 x = \frac{F}{m}$$

or polarization

$$\frac{d^2P}{dt^2} + \sigma \frac{dP}{dt} + \omega_0^2 P = \omega_0^2 \varepsilon \chi_0 \mathcal{E}$$



Coupled oscillators



zero crossing

absorption resonance

Low frequencies $\chi \sim \chi_0$

above resonance $\chi' \to 0$, $\chi'' \to 0$ ("free space")

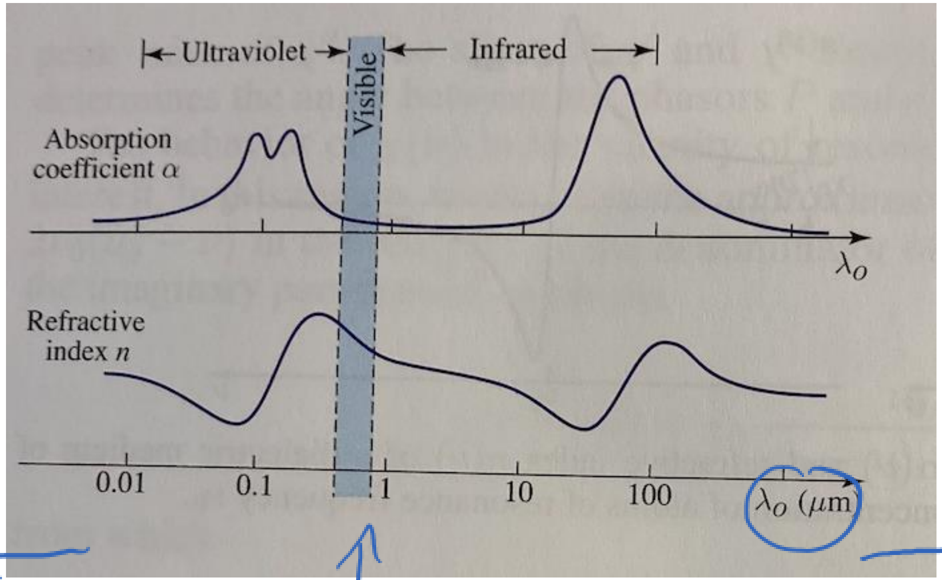
→ no/weak absorption

A real optical (transparent) material

X-rays

↓

core electrons



frequency

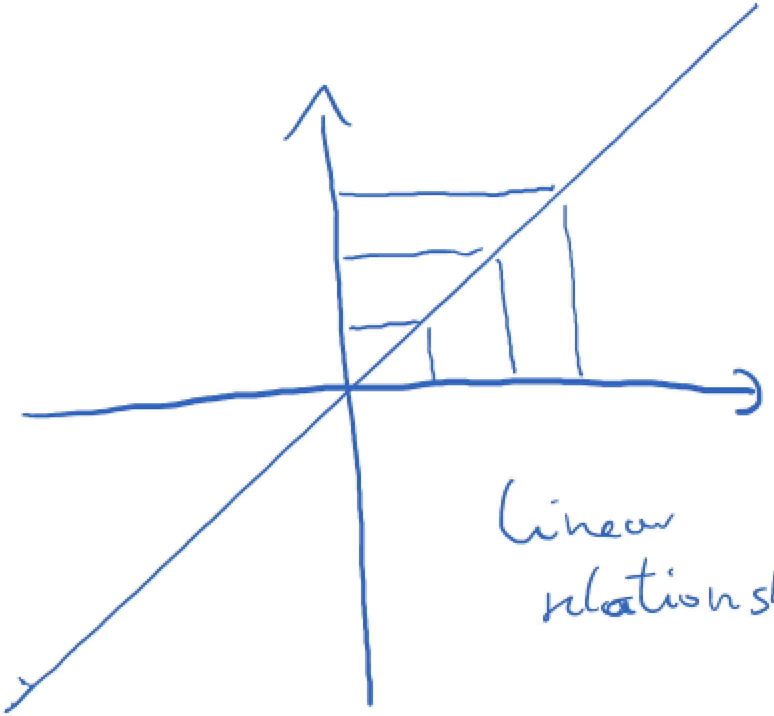
wavelength

your experience

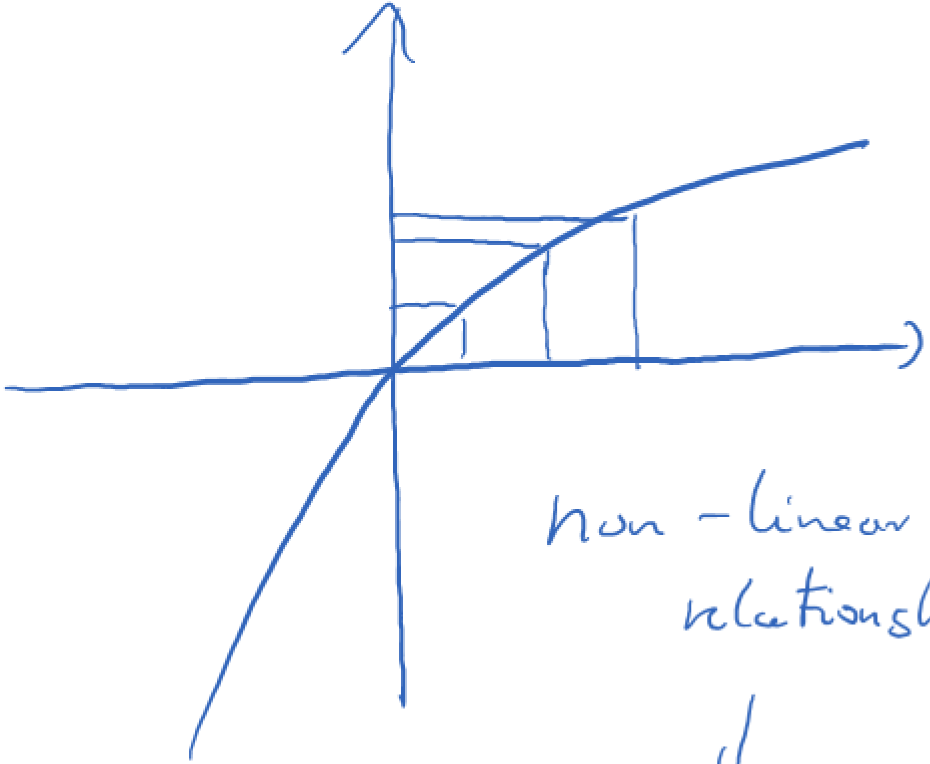
bottom line: a material is never really fully transparent

→ "simple" refractive index works only in selected regimes

From linear to non-linear



linear relationship



non-linear relationship

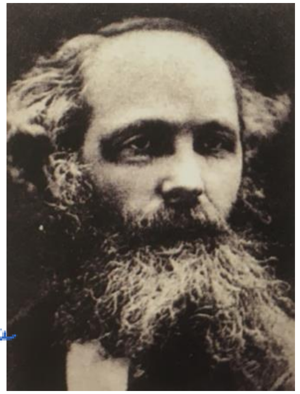
↓

Taylor expansion

↓

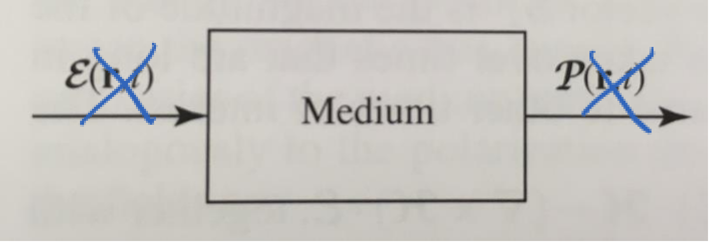
wonderful things will happen

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



James Maxwell
1831 - 1879

back then: dielectric, homogenous... medium



Maxwell in vacuum

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

Maxwell in dielectric media

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

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

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

P – polarization density
Σ dipole moments
induced by electric field
Ok for most cases

Susceptibility
$\mathcal{E} \to \boxed{\chi} \to P$

$$\nabla^2 u - \frac{1}{c^2}\frac{\partial^2}{\partial t^2} = 0$$
$$n = c_o/c = \sqrt{\frac{\varepsilon}{\varepsilon_o}\frac{\mu}{\mu_o}}$$
non magnetic
$$n = \sqrt{\varepsilon/\varepsilon_o}$$

Generalization of susceptibility $\mathbf{X}$ (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:

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

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

$\rightarrow$ light induced distortion

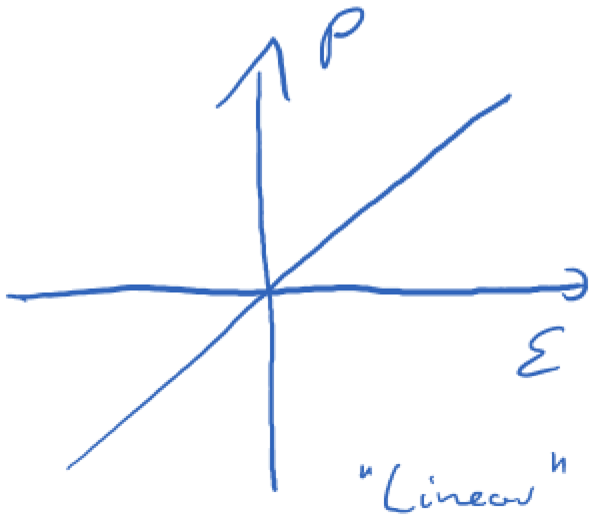
$\Downarrow$

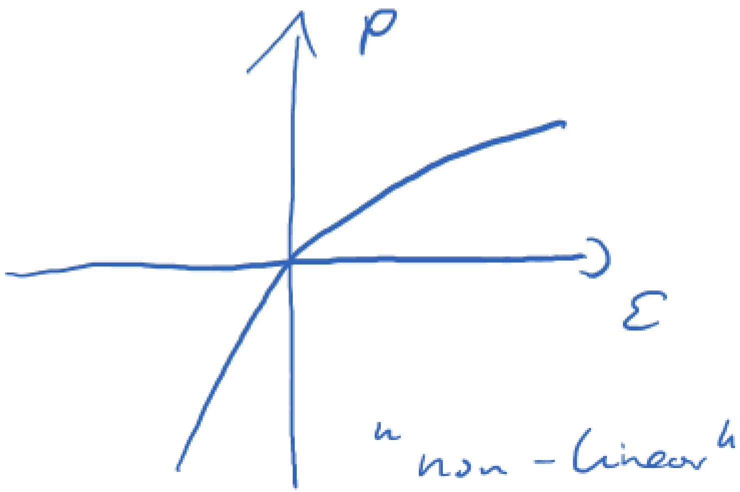
Lorentz oscillator model

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)





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

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

Generally $P = \varepsilon_0 \chi E$ χ – assume details unknown

Solution Taylor expansion

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

Linear — 2nd order non-linearity — 3rd order non-linearity

Second order non-linear optics example: Second harmonic generation

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

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

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

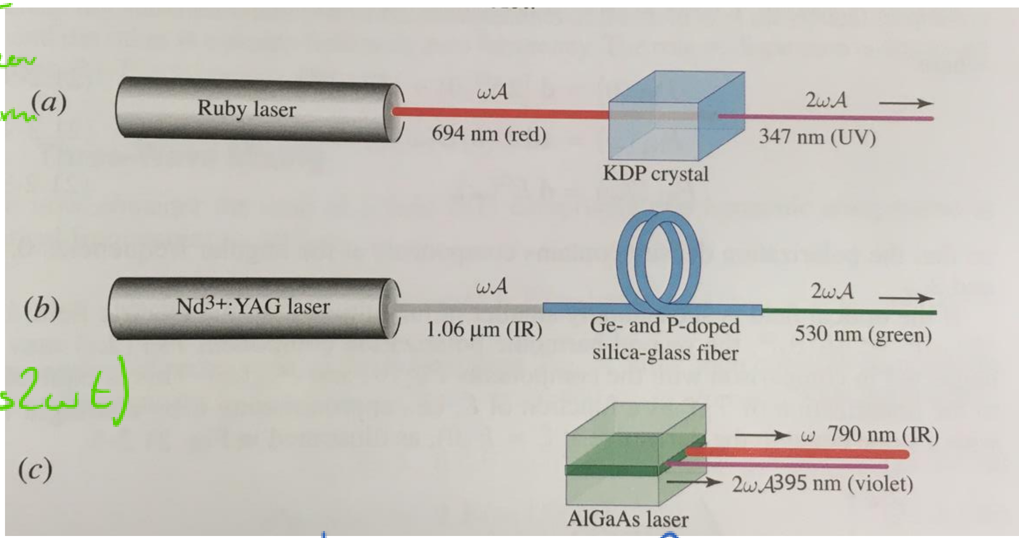
$P = \varepsilon_0 \chi \mathcal{E}_0 \sin \omega t$
$+ \varepsilon_0 \chi_2 \mathcal{E}_0^2 \sin^2 \omega t$
$+ \dots$

non-linear term

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

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

new frequency component!



use "non linear" crystals

Note

you can also expand Maxwells equations into non-linear regime

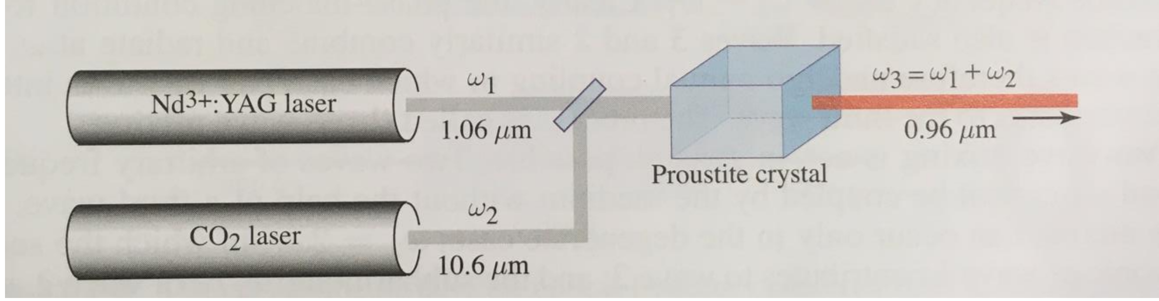
Second order non-linear optics example: Sum frequency generation

(three wave mixing)

$\mathcal{E} = \mathcal{E}_{01} \sin \omega_1 t + \mathcal{E}_{02} \sin \omega_2 t$ (two frequencies / waves)

Look only at squared term:

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



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

$\Rightarrow$ frequency up / down conversion

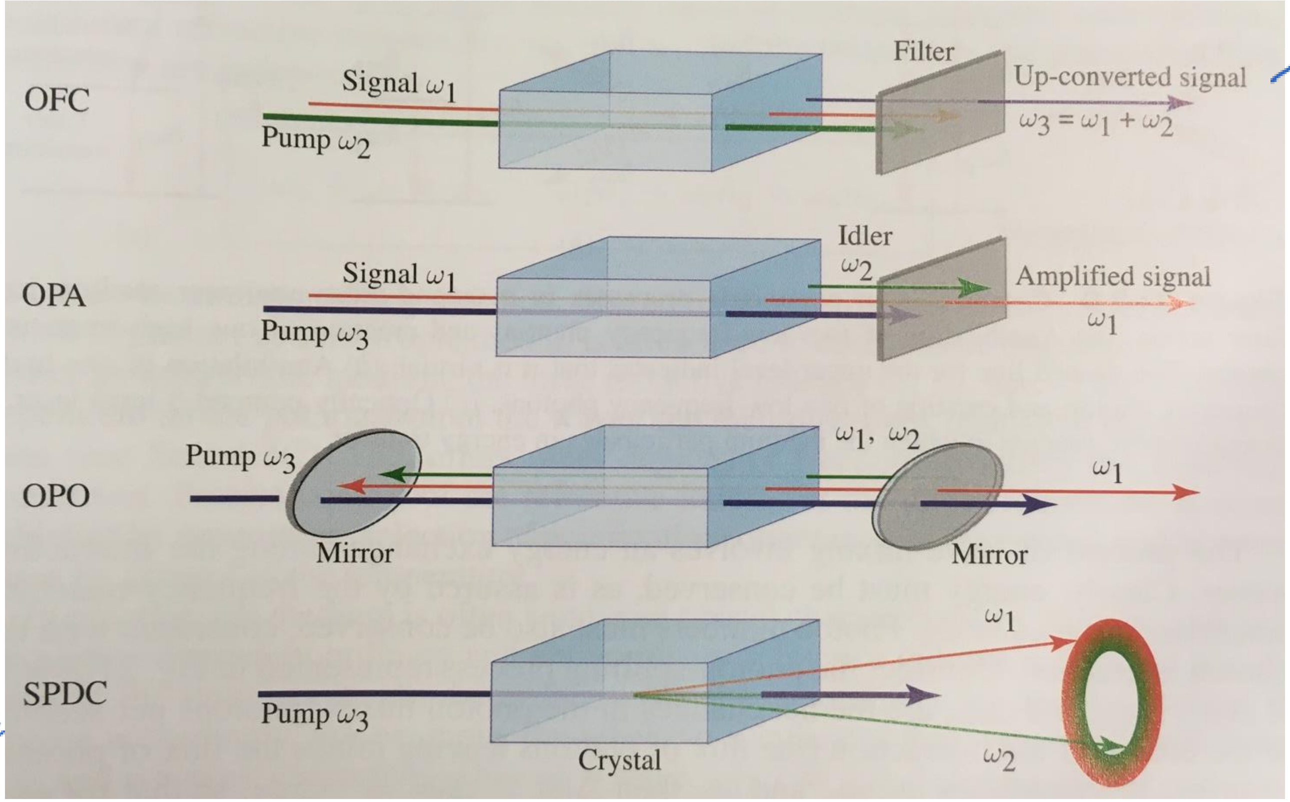
Second order non-linear optics example: Optical parametric devices

Optical frequency conversion

Optical parametric amplifier

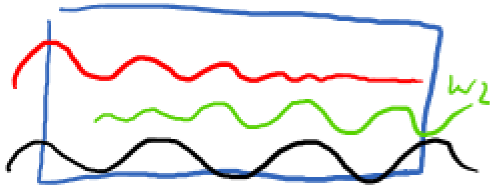
... oscillator

Spontaneous parametric conversion



Sum frequency conversion

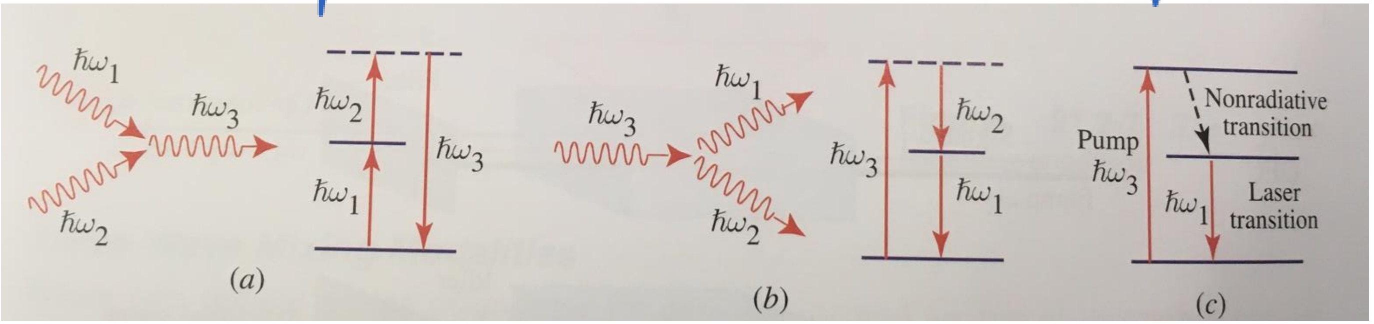
wave 1 & 3 interact and create wave 2



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

always maintain momentum & energy conservation

up down parametric process



here medium participates in energy / moment transfer

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

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

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

↳ in principle the same with next term

↳ could also generate 3ω light but conversion efficiency low

⇓

if you want higher frequency light

then approach of 2^{nd} harmonic generation + frequency mixing } $2\times$ 2^{nd} order process

can be better

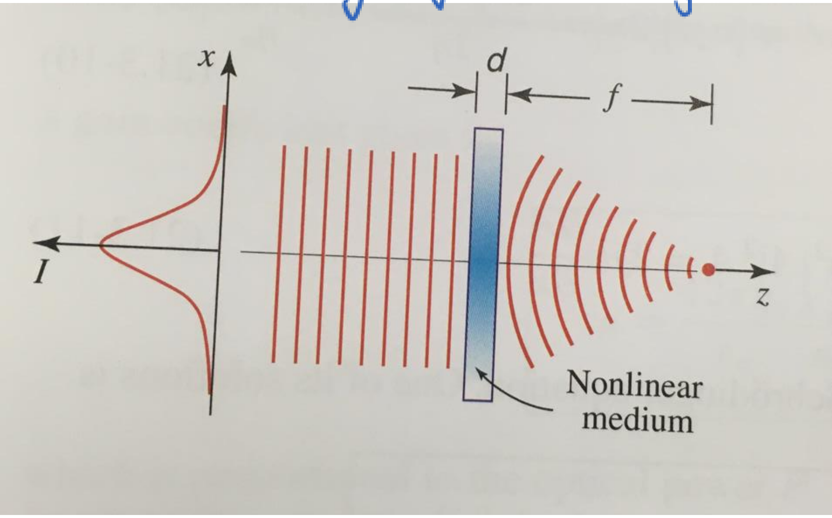
Third order non-linear optics example: Optical Kerr Effect and Self-Focusing

You can show that in 3rd order non-linearities you can get intensity-dependent refractive index

$$n(I) = n + n_2 I$$

optical Kerr effect

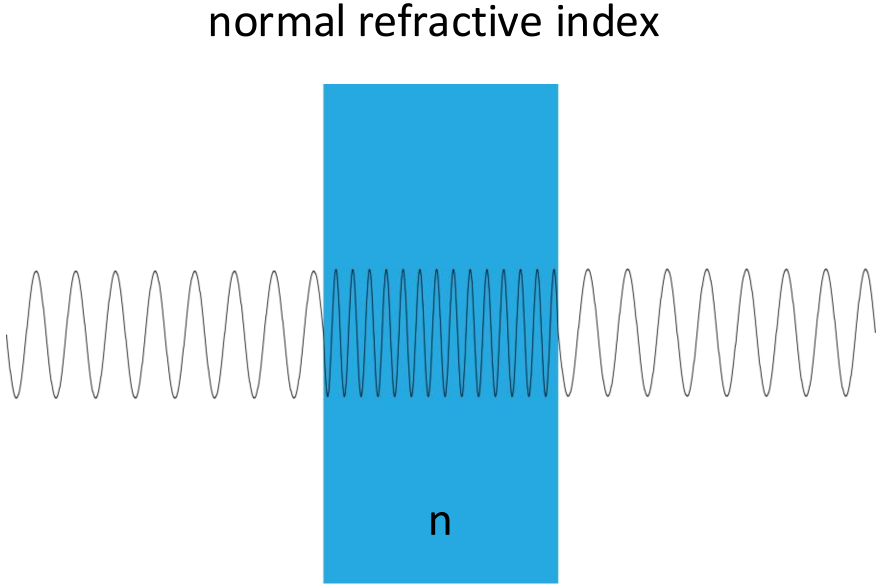
"self focussing"

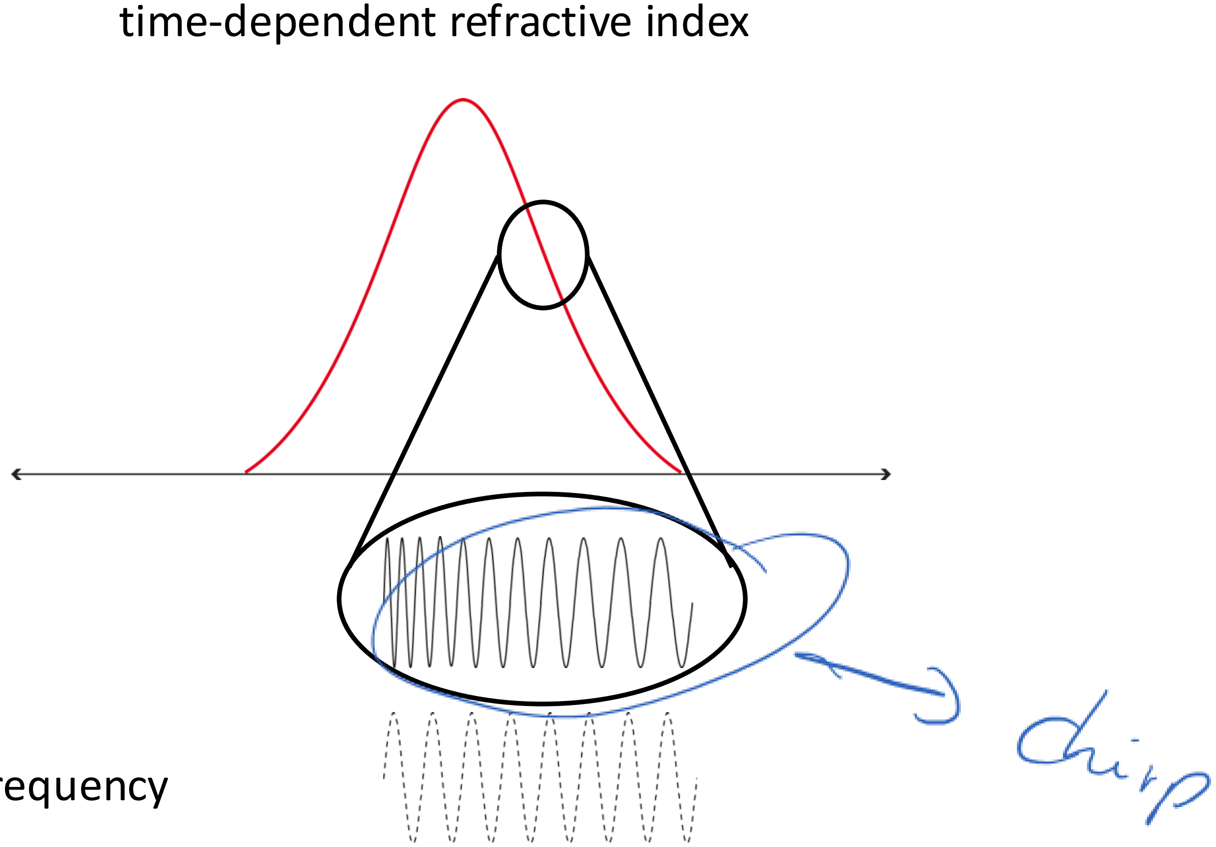


$\Rightarrow$ now you can use light pulse to change optical properties itself

$\Rightarrow$ Gaussian beam $\rightarrow$ intensity dependent lens!

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





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

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

The end.