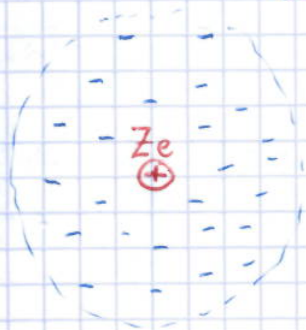
CLASSICAL LIGHT-MATER INTERACTION IN A DIELECTRIC MEDIUM - SPECTROSCOPY

1) Macroscopic description

a) Bound charges - Dielectric volumic polarization

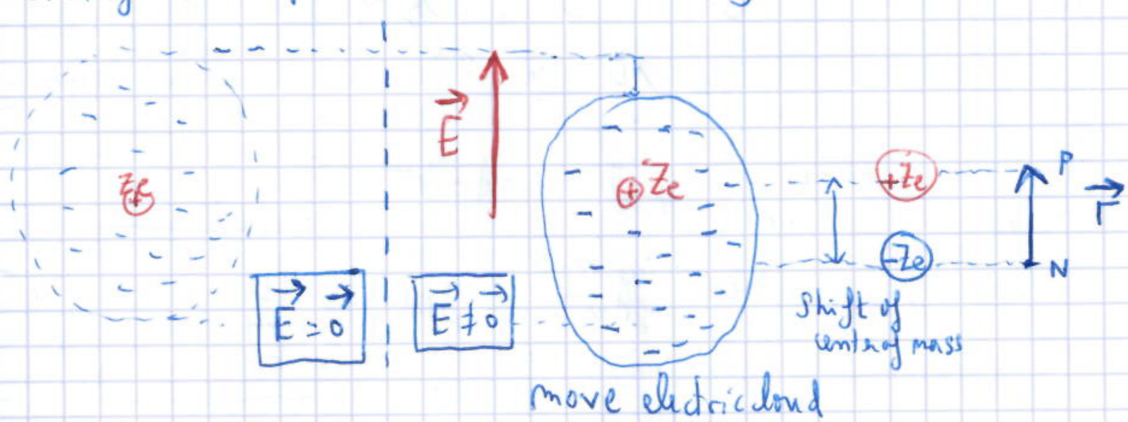
1 atom = electricaly neutral but not spatially.

- $+Ze$: nucleus and Z e^- around



Electronic cloud and center of mass of positive charge $+Ze$ = center of mass of Z negative charges : $-Ze$

- Action of electric field $\vec{E}$ (can be the light).



move electric cloud

→ creation of an electrostatic dipole $\vec{p} = q\,\vec{NP}$

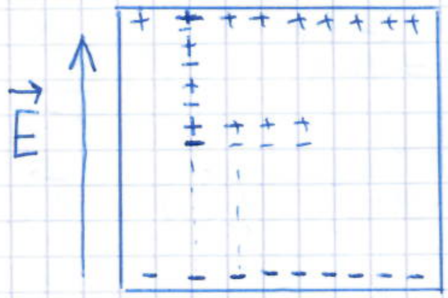
→ q is not equal to $|Ze|$ due to screening effects.

→ motion of charge over a small distance

$$\vec{p}_i = q\,\vec{r}_i$$

$$\frac{d\vec{p}_i}{dt} = q\,\frac{d\vec{r}_i}{dt} = \vec{j}_i \quad \text{small current.}$$

For all material:



i) Polarisation of matter related to electric field perturbation

ii) Volumic polarization $\vec{P} = \frac{1}{V} \sum_{i=1}^{N} \vec{p_i} \equiv \varepsilon_0 \chi \vec{E}$

- χ is dielectric susceptibility.

iii) total polarization current $\vec{J_{pol}}$ or $\vec{J_{bound}} = \frac{1}{V} \sum_{i=1}^{N} \vec{j_i} = \sum_{i=1}^{N} \frac{dp_i}{dt}$

and: $$\vec{J_{bound}} = \frac{d}{dt}\left[\sum_{i=1}^{N} \vec{p_i}\right] \cdot \frac{1}{V} = \frac{d}{dt}\vec{P}$$

$$\left.\begin{aligned} &\vec{\nabla} \cdot \vec{J_{bound}} + \frac{\partial \rho_{bound}}{\partial t} = 0 \\ &\vec{\nabla} \cdot \frac{\partial \vec{P}}{\partial t} + \frac{\partial \rho_{bound}}{\partial t} = 0 \\ &\frac{\partial}{\partial t}\left[\vec{\nabla} \cdot \vec{P}\right] = -\frac{\partial}{\partial t} \rho_{bound} \end{aligned}\right\} \quad \rho_{bound} = -\vec{\nabla} \cdot \vec{P} = -\operatorname{div} \vec{P}$$

We keep: $$\boxed{\begin{aligned} \vec{J_{pol}} &= \vec{J_{bound}} = \frac{\partial \vec{P}}{\partial t} \\ \rho_{pol} &= \rho_{bound} = -\operatorname{div} \vec{P} \end{aligned}}$$

current and charge densities of bound charges (or polarised charges) are connected to the volumic Polarization

b- Maxwell equations and wave equation

$$\operatorname{div}\vec{E} = \frac{\rho}{\varepsilon_0} \qquad \operatorname{div}\vec{B} = 0$$

$$\vec{rot}\,\vec{E} = -\frac{\partial\vec{B}}{\partial t} \qquad \vec{rot}\,\vec{B} = \mu_0\vec{j} + \mu_0\varepsilon_0\frac{\partial\vec{E}}{\partial t}$$

$$\rho = \underbrace{\rho_{free}}_{\downarrow\, 0} + \rho_{bound} \quad ; \quad \vec{j} = \underbrace{\vec{j}_{free}}_{\downarrow\, 0} + \vec{j}_{bound} + \underbrace{\vec{j}_{mag}}_{\downarrow\, 0}$$

in dielectrics:

i) $$\operatorname{div}\vec{E} = \frac{\rho}{\varepsilon_0} = \frac{\rho_{free}+\rho_{bound}}{\varepsilon_0} = \frac{\rho_{bound}}{\varepsilon_0}$$

$$\operatorname{div}(\varepsilon_0\vec{E}) = \rho_{bound} = -\operatorname{div}\vec{P}$$

$$\operatorname{div}(\varepsilon_0\vec{E} + \vec{P}) = 0 \qquad \text{and } \vec{P} = \varepsilon_0\chi\vec{E}$$

$$\operatorname{div}(\varepsilon_0\vec{E} + \varepsilon_0\chi\vec{E}) = 0$$

$$\operatorname{div}(\varepsilon_0\underbrace{(1+\chi)}_{\varepsilon_r}\vec{E}) = 0$$

$$\operatorname{div}(\varepsilon_0\varepsilon_r\vec{E}) = 0.$$

$$\boxed{\varepsilon_0\varepsilon_r\operatorname{div}\vec{E} = 0}$$

ii) $$\vec{rot}\,\vec{B} = \mu_0\vec{j} + \mu_0\varepsilon_0\frac{\partial\vec{E}}{\partial t} = \mu_0\frac{\partial\vec{P}}{\partial t} + \mu_0\varepsilon_0\frac{\partial\vec{E}}{\partial t}$$

$$= \mu_0\frac{\partial}{\partial t}\left[\vec{P} + \varepsilon_0\vec{E}\right] = \mu_0\frac{\partial}{\partial t}\left[\varepsilon_0(1+\chi)\vec{E}\right]$$

$$= \mu_0\frac{\partial}{\partial t}\varepsilon_0\varepsilon_r\vec{E} = \boxed{\mu_0\varepsilon_0\varepsilon_r\frac{\partial\vec{E}}{\partial t} = \vec{rot}\,\vec{B}}$$

Wave equation:

$$\left.\begin{array}{l} \vec{rot}\,\vec{E} = -\dfrac{\partial\vec{B}}{\partial t} \\[2ex] \vec{rot}\,\vec{B} = \mu_0\varepsilon_0\varepsilon_r\dfrac{\partial\vec{E}}{\partial t} \end{array}\right\} \quad \begin{array}{l} \vec{rot}\,\vec{rot}\,\vec{E} = \vec{grad}\operatorname{div}\vec{E} - \Delta\vec{E} = -\dfrac{\partial}{\partial t}\vec{rot}\,\vec{B} \\[2ex] \dfrac{\partial}{\partial t}\vec{rot}\,\vec{B} = \mu_0\varepsilon_0\varepsilon_r\dfrac{\partial^2\vec{E}}{\partial t^2} \end{array}$$

$$\underbrace{\vec{grad}\, div \vec{E}}_{0} - \Delta \vec{E} = -\mu_0 \varepsilon_0 \varepsilon_r \frac{\partial^2 \vec{E}}{\partial t^2}$$

$\varepsilon_0 \varepsilon_r \, div \vec{E} = 0.$

We obtain a wave equation:

$$\Delta \vec{E} - \mu_0 \varepsilon_0 \varepsilon_r \frac{\partial^2 \vec{E}}{\partial t^2} = 0$$

$$\Delta \vec{E} - \frac{\varepsilon_r}{c^2} \frac{\partial^2 \vec{E}}{\partial t^2} = 0 \quad \text{with } v = \frac{c}{\sqrt{\varepsilon_r}} = \frac{c}{n}$$

$\sqrt{\varepsilon_r} = n$ optical index

$\sqrt{\varepsilon_r} = \sqrt{1+\chi}.$

c. Solution - dispersion and absorption.

$\vec{E} = E_0 \cos(-\omega t + \vec{k}\cdot\vec{r})$ or

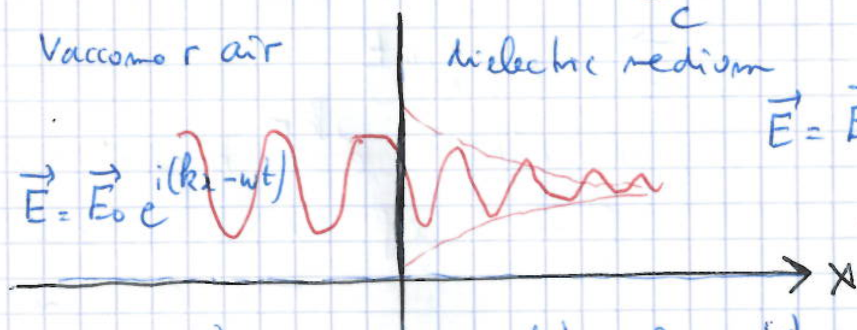
$\underline{\vec{E}} = \underline{E_0}\, e^{i(-\omega t + \vec{k}\cdot\vec{r})}$ plug in W eq to get

$$-k^2 + \frac{\varepsilon_r}{c^2} \omega^2 = 0.$$

$$v_\varphi = \frac{\omega}{k} = \frac{c}{\sqrt{\varepsilon_r}} \quad \text{and} \quad k = \frac{\sqrt{\varepsilon_r}\,\omega}{c} = \frac{n\omega}{c}$$

At 1 dim: $\vec{k}\cdot\vec{r} = kx = \frac{n\omega}{c} . x.$

Vaccum or air | dielectric medium



$\vec{E} = \vec{E_0} e^{i(kx - \omega t)}$

$$\vec{E} = \vec{E_0} \underbrace{e^{-k''x}}_{\text{attenuation}} \underbrace{e^{i(k'x - \omega t)}}_{\text{propagation}}$$

In next § $n \in \mathbb{C}$: $\underline{n}^{(\omega)} \mapsto \underline{k} = \frac{\underline{n}^{(\omega)} \omega}{c} = \underset{\text{real}}{k'(\omega)} + i \underset{\text{imaginary}}{k''(\omega)}$

$$e^{ikx} = e^{ik'x} \cdot e^{iik''x} = e^{ik'x} e^{-k''x}$$

→ real part of k: $k'(\omega)$ is $k'(\omega) = \frac{n'(\omega)\omega}{c}$

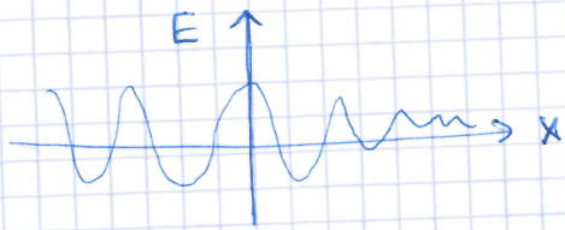
→ <u>dispersion</u>: phase velocity is different for each frequency

→ imaginary part: $k''(\omega) \rightarrow e^{-k''(\omega)x}$

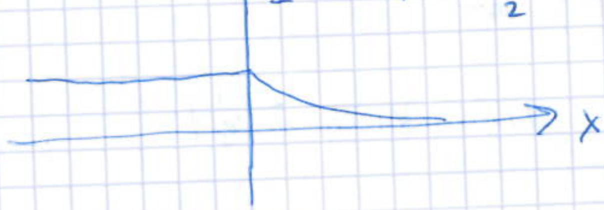
intensity: $I \sim E^2 \sim E \cdot E^*$

$$I \sim E_0^2 \, e^{-2k''(\omega)x}$$

$$I \sim I_0 \, e^{-\alpha x}$$ Beer-Lambert law.



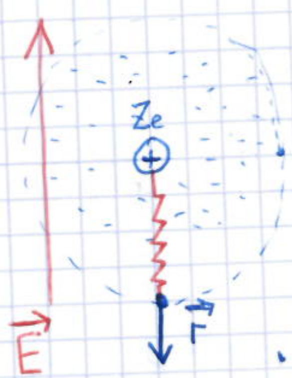
$I \sim \langle E^2 \rangle \sim \frac{E_0^2}{2} e^{-2\alpha x}$



2. Microscopic description.

a. Electron elastically "bound to the nucleus" driven oscillator

Electronic atom submitted to an e-m wave.



• $\vec{E} = E_0 e^{+i\omega t}$

We neglect e^{ikr} because $kx = \frac{2\pi}{\lambda} r$

$\frac{r}{\lambda} \ll 1$ if $\lambda \sim \lambda_{optics, UV} \sim 10^{-7}$ m

$r \sim d_{atom} \sim 10^{-10}$ m.

• electron can not escape - due to electrostatic force originating from other electrons and the nucleus

elastic $\vec{force} = -k\vec{r} = -m\omega_0^2 \vec{r}$

- Origin of $-k\vec{r}$: e^- is like living inside a sphere charged in volume:

Gauss therem inside the sphere give $E = \frac{\rho r}{3\varepsilon_0}$ so $\vec{F} = q\vec{E} \sim r$

- Lorentz force $\vec{F} = q(\vec{E} + \vec{v} \times \vec{B}) = q\left(\vec{E} + \vec{v} \times \vec{u}\left|\frac{E}{c}\right|\right)$

  but $v \ll c$ so magnetic force is neglegted.

$$\vec{F} = q\vec{E}$$

- Existence of a "damping force" due to energy lost during motion: (emission - collision)

  phenomenolgical description: $\vec{f} = -\frac{m}{\tau}\vec{V}$ with τ characteristic time

2^nd^ Newton law: $m\vec{a} = \Sigma \vec{\text{forces}}$

$$m\ddot{\vec{r}} = q\vec{E} - m\omega_0^2\vec{r} - \frac{m}{\tau}\vec{V}$$

Driven Oscillator with

$$\left.\begin{aligned} \vec{r} &= r_0 e^{+i\omega t} \\ \dot{\vec{r}} &= \vec{V} = i\omega\vec{r} \\ \ddot{\vec{r}} &= -\omega^2\vec{r} \end{aligned}\right\}$$

$$-m\omega^2\vec{r} = q\vec{E} - m\omega_0^2\vec{r} - i\frac{\omega}{\tau}m\vec{r}$$

$$\left(\omega_0^2 - \omega^2 + \frac{i\omega}{\tau}\right)\vec{r} = \frac{q}{m}\vec{E}$$

$$\boxed{\vec{r} = \frac{q}{m}\frac{\vec{E}}{\left[\omega_0^2 - \omega^2 + \frac{i\omega}{\tau}\right]} = \vec{r}(\omega, E)}$$

amplitude depends on the frequency and the electric field amplitude

b) Expression of the volumic Polarization - dielectric susceptibility

$\cdot\ \vec{p} = q\vec{r} = q\,\vec{r}(\omega, \vec{E})$ 1 dipole

$\cdot\ \vec{P} = \frac{1}{V}\sum_{i=1}^{N} \vec{p_i} = \frac{N}{V}\vec{p} = n_v \vec{p}$

$$= \frac{n_v q^2 \vec{E}}{m\left[\omega_0^2 - \omega^2 + \frac{i\omega}{\tau}\right]} \times \frac{\varepsilon_0}{\varepsilon_0}$$

$$= \varepsilon_0 \left[\frac{n_v q^2}{m\varepsilon_0\left[\omega_0^2 - \omega^2 + \frac{i\omega}{\tau}\right]}\right]\vec{E} \equiv \varepsilon_0 \chi \vec{E}$$

$$\boxed{\chi(\omega) = \frac{n_v q^2}{m\varepsilon_0\left[\omega_0^2 - \omega^2 + \frac{i\omega}{\tau}\right]} = \frac{\omega_p^2}{\left[\omega_0^2 - \omega^2 + \frac{i\omega}{\tau}\right]}}$$

with $\omega_p^2 = \frac{n_v q^2}{m\varepsilon_0}$: plasma pulsation.

Frequency dependance of dielectric susceptibility.

c) Frequencies dependance of dielectric functions

- $\chi(\omega) = \underbrace{\chi'(\omega)}_{\text{real}} + i\underbrace{\chi''(\omega)}_{\text{imaginary}}$ is a complex function
- by multiplying by complex conjugate of denominator up and down we obtain

$$\chi(\omega) = \frac{\omega_p^2 \left[\omega_0^2 - \omega^2 - i\omega/\tau\right]}{\left[\omega_0^2 - \omega^2 + \frac{i\omega}{\tau}\right]\left[\omega_0^2 - \omega^2 - \frac{i\omega}{\tau}\right]}$$

3) Applications in Spectroscopy.

a- differents order size dipoles and total dispersion / absorption spectrum

→ $\varepsilon_r(\omega) = 1 + \chi(\omega) = n^2(\omega)$.

⇒ $n(\omega)$ is a complex function:

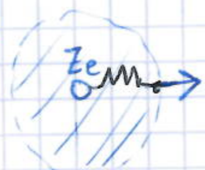
optical index depends on ω (or λ).

→ Which λ is playing an important role:

→ Many "oscillators"

$\omega_0 \approx \sqrt{\frac{k}{m}}$

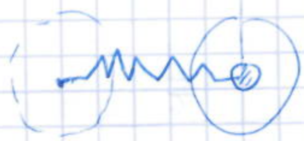
→ electronic polarization:



$\omega_{0_e} \sim 10^{15} \sim 10^{16}\ s^{-1}$

$E_{photon} \approx \hbar\omega_0$.

→ ionic polarization



$\omega_{0_i} \sim 10^{12}\ s^{-1}$

$m_{atome} \gg m_{e^-}$

→ orientation polarization:

$\chi(\omega) \approx \frac{1}{1 + \omega^2 \tau^2}$

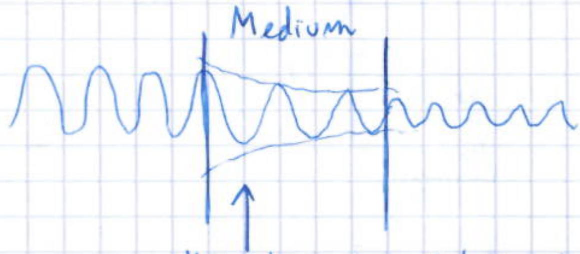
Contribution of all phenomena.

→ slides $\chi'(\omega)$ dispersion

→ water $\varepsilon_r = 80$ (Low frequency)

$n_{LF} \approx$ and $n_{optic_{HF}} \approx 1{,}333$ (high frequency)

b- Beer-Lambert law



- attenuation of amplitude depends on ω (or λ) it is maximum at ω_0: $\vec{E} = \vec{E_0} e^{-k''x} e^{i(\omega t - k'x)}$ $\quad k = n k_0$ (↓ in vacuum)

with $k''(\omega) = n''(\omega) k_0 = n''(\omega) \frac{\omega}{c}$

$$I \approx \langle \vec{E} \cdot \vec{E}^* \rangle \approx \frac{E_0^2}{2} e^{-2k''x} = I_0 e^{-2k''x}$$

$$\ln \frac{I}{I_0} = -2k''x \Leftrightarrow A = \ln \frac{I_0}{I} = 2k''x$$

After crossing distance L

$$A = 2k''L = \text{"} c\, \varepsilon L \text{"}$$

$$2k'' = 2n''(\omega) = c\, \varepsilon(\omega)$$

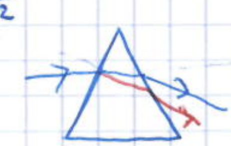
concentration → related to n_v in ω_p^2

c- Dispersion and Cauchy law:

- In dielectric $n = n(\omega) = n_0 + \frac{C}{\lambda^2}$
- Example prism:

blue $\lambda = 488\,nm$ $\quad n_b = 1,518$

red $\lambda = 632,8\,nm$ $\quad n_r = 1,505$



We look $\chi'(\omega) = \frac{\omega_p^2(\omega_0^2 - \omega^2)}{(\omega_0^2 - \omega^2)^2 + \cancel{\frac{\omega^2}{\tau^2}}}$ for $\omega \ll \omega_0$ we neglect absorption

$$\simeq \frac{\omega_p^2}{\omega_0^2 - \omega^2}$$

and $n^2 = 1 + \chi = \varepsilon_r \approx 1 + \chi'$

$$= 1 + \frac{\omega_p^2}{\omega_0^2 - \omega^2} \approx 1 + \frac{\omega_p^2}{\omega_0^2}\left(1 + \frac{\omega^2}{\omega_0^2}\right)$$

$$n = \left[1 + \frac{\omega_p^2}{\omega_0^2} + \underbrace{\frac{\omega_p^2}{\omega_0^4}\,\omega^2}_{\text{Small}}\right]^{1/2}$$

$$=$$

$$= \underbrace{1 + \frac{\omega_p^2}{\omega_0^2}} + \frac{\omega_p^2}{2\omega_0^4}\,\omega^2 \quad \text{and} \quad \omega = \frac{2\pi c}{\lambda}$$

$$= n_0 + \frac{C}{\lambda^2}$$

d)