Dispersion relations

Comparing the found relations between optical values (κ, n) with EM- values (ε, μ, σ) we observe discrepancies:

For example: For water we can measure a static dielectric function $\varepsilon_r = 81$, while the refractive index n is $4/3$.

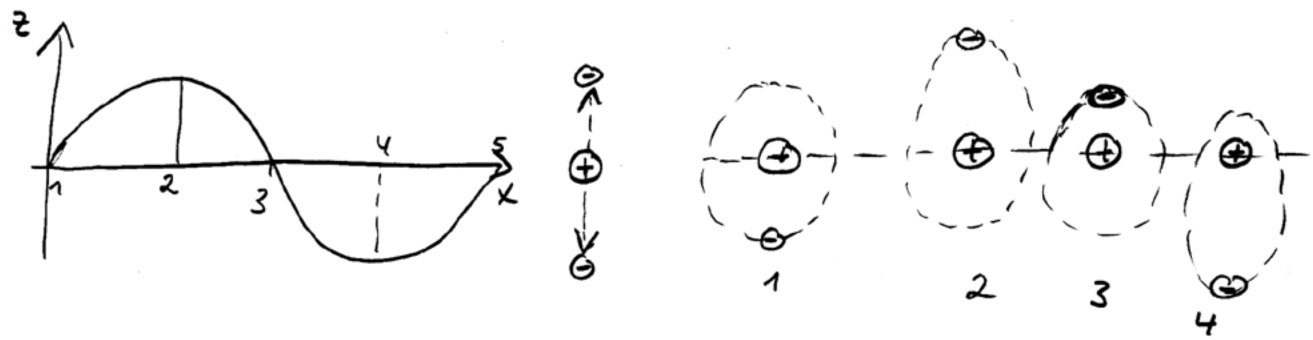
↳ optical constants ε, μ are frequency dependant, which is described in the dispersion relations!

(1) classical model: Drude - Lorentz model for $\varepsilon(\omega)$

(2) Quantum mechanical description for $\varepsilon(\omega)$

↳ Drude - Lorentz model for $\varepsilon(\omega)$

Assume a EM-wave interacts with matter (medium) consisting of bonded atoms and elastically bonded electrons e^-. The EM-wave and e^- interaction cases the displacement of the e^-



Displacement: $\Delta z(t) = \Delta z_{max} \cdot e^{-i\omega t} = z(t) - \vec{z}_0$ (1)

⟹

$\leadsto$ Equation of motion

$$② \quad m \cdot \frac{d^2}{dt^2} \Delta z + q \cdot \vec{E}_0 e^{-i\omega t} + b \cdot \frac{d}{dt} \Delta z(t) + K \cdot \Delta z(t) = 0$$

merge equ. ① into ②:

$$\hookrightarrow \left[-\omega^2 \Delta z_{max} - i\omega \cdot \frac{b}{m} \Delta z_{max} + \frac{K}{m} \Delta z_{max} + \frac{q}{m} \vec{E}_0 \right] \cdot e^{-i\omega t} = 0$$

$$\leadsto \Delta z_{max} = \frac{q/m}{\omega^2 - K/m + i\omega b/m} \cdot \vec{E}_0$$

Now; we now the macroscopic Polarization is

$$P = (\varepsilon_r - 1)\varepsilon_0 \vec{E} \overset{!}{=} - n \cdot q \cdot \Delta z(t)$$

charge per atom

# of atoms

$$\leadsto P(t) = - n q \cdot \Delta z(t) = \frac{- n q^2/m}{\omega^2 - \omega_0^2 + i\omega/\tau} \cdot \vec{E}_0 e^{-i\omega t} \quad \left| \begin{array}{l} \omega_0^2 = K/m \\ \tau = m/b \end{array} \right.$$

$$= (\varepsilon_r - 1)\varepsilon_0 \vec{E}$$

define $\omega_p = \sqrt{\frac{n \cdot q^2}{\varepsilon_0 \cdot m}}$: plasma frequency

to get

$$\boxed{\varepsilon_r(\omega) = 1 - \frac{\omega_p^2}{\omega^2 - \omega_0^2 + i\omega/\tau}}$$

$\Rightarrow$

Limiting properties of dielectric function

$$\lim_{\omega \to 0} [\varepsilon(\omega) - 1] = \frac{\omega_p^2}{\omega_0^2} \qquad \text{(static dielectric function)}$$

$$\lim_{\omega \to \infty} [\varepsilon(\omega) - 1] = \lim_{\omega \to \infty} \left(-\frac{\omega_p^2}{\omega_0^2} \right) = 0$$

$\hookrightarrow$ $[\varepsilon(\omega) - 1]$ converges as $\frac{1}{\omega^2}$

Separate ε into real- and imaginary part:

a.) rewrite $\omega^2 - i\omega/\tau - \omega_0^2 = [\omega - \omega_1 + i\Gamma] \cdot [\omega + \omega_1 + i\Gamma]$

$$= \omega^2 + i\, 2\omega\Gamma - (\omega_1^2 + \Gamma^2)$$

So that $\omega_1 = \sqrt{\omega_0^2 - \Gamma^2}$ and $\Gamma = 1/2\tau$ (Γ: broadening parameter)

b.) take identity $\frac{f_1(x) - f_2(x)}{f_1(x) \cdot f_2(x)} \equiv \frac{1}{f_2(x)} - \frac{1}{f_1(x)}$

to separate in partial fractions

$$\varepsilon(\omega) = 1 + \frac{\omega_p^2}{(\omega - \omega_1 + i\Gamma)(\omega + \omega_1 + i\Gamma)}$$

$$= 1 + \frac{\omega_p^2}{2\omega_1} \left[\frac{1}{\omega + \omega_1 + i\Gamma} - \frac{1}{\omega - \omega_1 + i\Gamma} \right]$$

$\Longrightarrow$

$\rightsquigarrow$ For small damping: $\omega_0^2 \gg \Gamma^2$ $\rightsquigarrow$ $\omega_1 \to \omega_0$

$$\hookrightarrow \quad \varepsilon(\omega) = 1 + \frac{\omega_p^2}{2\omega_0}\left[\frac{1}{\omega+\omega_0+i\Gamma} - \frac{1}{\omega-\omega_0+i\Gamma}\right]$$

next, multiply first term in bracket with $\frac{\omega+\omega_0-i\Gamma}{\omega+\omega_0-i\Gamma}$ and second term with $\frac{\omega-\omega_0-i\Gamma}{\omega-\omega_0-i\Gamma}$ to get

$$\varepsilon(\omega) = 1 + \frac{\omega_p^2}{2\omega_0}\left[\frac{\omega+\omega_0}{(\omega+\omega_0)^2+\Gamma^2} - \frac{\omega-\omega_0}{(\omega-\omega_0)^2+\Gamma^2}\right] - i\,\frac{\omega_p^2\Gamma}{2\omega_0}\left[\frac{1}{(\omega+\omega_0)^2+\Gamma^2} - \frac{1}{(\omega-\omega_0)^2+\Gamma^2}\right]$$

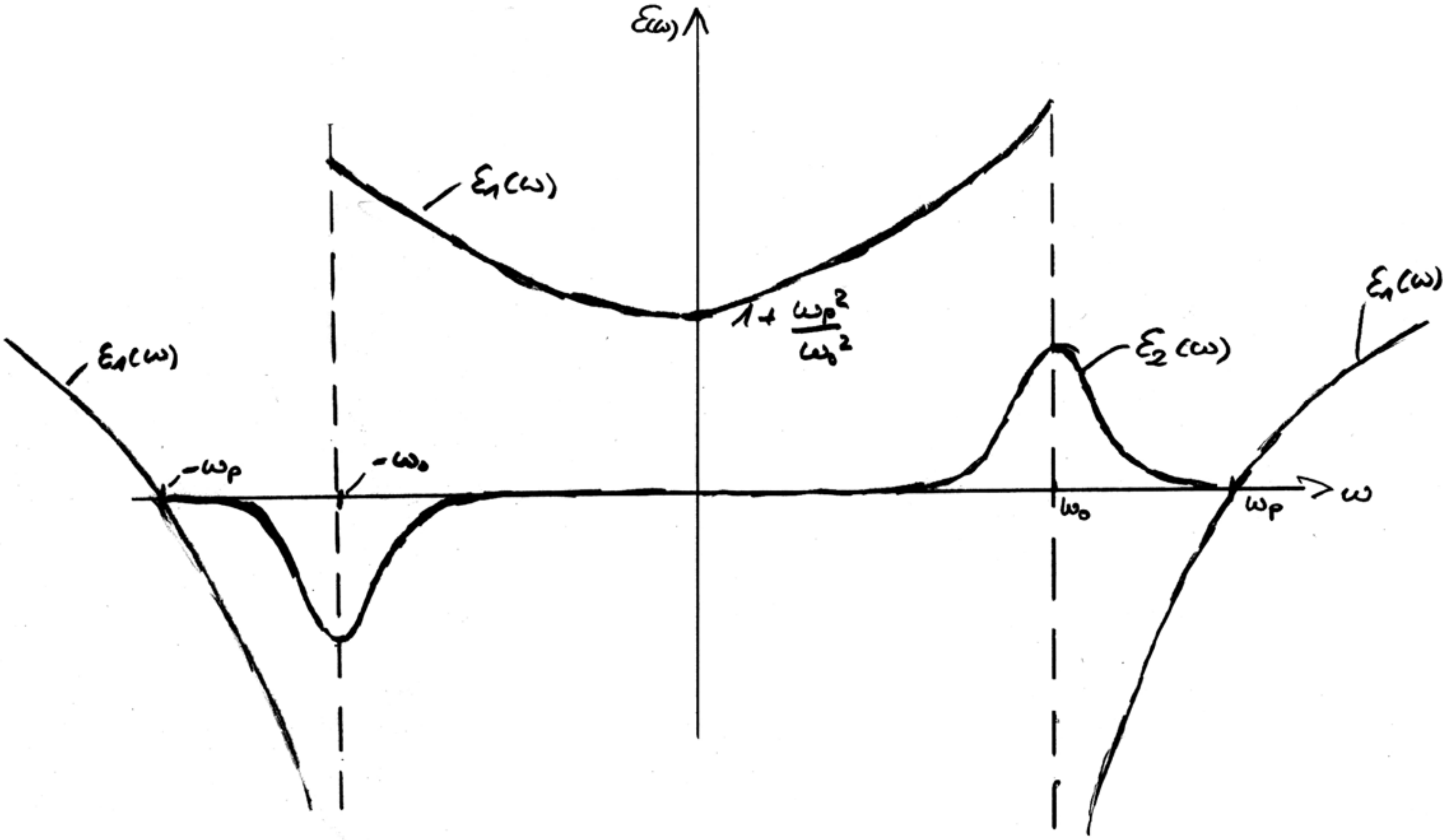
$$= \varepsilon_1 + i\,\varepsilon_2$$

$$\hookrightarrow \quad \boxed{\begin{aligned} \varepsilon_1 &= 1 + \frac{\omega_p^2}{2\omega_0}\left[\frac{\omega+\omega_0}{(\omega+\omega_0)^2+\Gamma^2} - \frac{(\omega-\omega_0)}{(\omega-\omega_0)^2+\Gamma^2}\right] \\ &\text{and} \\ \varepsilon_2 &= \frac{\omega_p^2\Gamma}{2\omega_0}\left[\frac{1}{(\omega+\omega_0)^2+\Gamma^2} - \frac{1}{(\omega-\omega_0)^2+\Gamma^2}\right] \end{aligned}}$$

that is

$$\varepsilon_1(\omega) = \varepsilon_1(-\omega) \qquad : \text{ an even function}$$

$$-\varepsilon_2(\omega) = \varepsilon_2(-\omega) \qquad : \text{ an odd function}$$



General properties of $\varepsilon(\omega)$:

Reality of $\vec{E}$ and linearity of $\vec{D}$

$$\vec{E}(\omega) = \vec{E}^*(-\omega)$$

$$\vec{D}(\omega) = \vec{D}^*(-\omega) = \varepsilon \cdot \vec{E}(\omega)$$

$$\varepsilon_1(\omega) = \varepsilon_1(-\omega) \quad \text{and} \quad \varepsilon_2(\omega) = -\varepsilon_2(-\omega)$$

Periodicity of $\vec{E}(t)$ and $\vec{P}(t) = \varepsilon_0 [\varepsilon - 1] \vec{E}(t)$

$$= \varepsilon_0 \int_{-\infty}^{\infty} P(\omega)\, e^{-i\omega t}\, d\omega$$

$\Rightarrow$

Use inverse Fourier transform

$$\vec{E}(\omega) = 2\epsilon_0 \int_{-\infty}^{\infty} E(t)\, e^{i\omega t'}\, dt' \quad \text{to get}$$

$$P(t) = \frac{\epsilon_0}{2\pi} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} [\epsilon(\omega) - 1]\, e^{-i\omega(t-t')}\, d\omega\, \vec{E}(t')\, dt$$

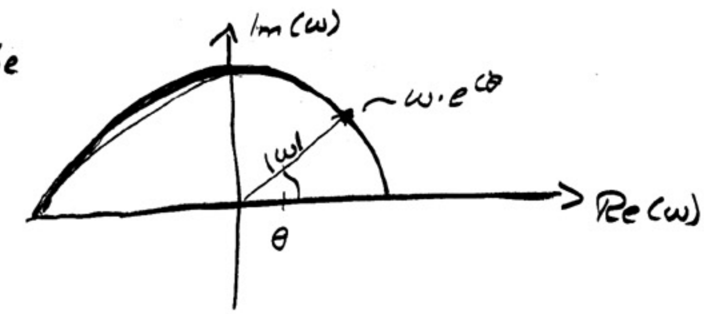
$$= \int_{-\infty}^{\infty} G(t-t')\, E(t')\, dt \quad \text{with the Green's function}$$

$$G(t-t') = \frac{\epsilon_0}{2\pi} \int_{-\infty}^{\infty} [\epsilon(\omega) - 1]\, e^{+i\omega(t'-t)}\, d\omega$$

Since the polarization $\vec{P}(\omega)$ is a response to the exciting EM-wave $\vec{E}(\omega)$, by causality

$$\boxed{G(t'-t) \equiv 0} \quad \text{for } t' > t$$

In the next step, we replace the integration path by a closed path in the limit $|\omega| \to \infty$



$$\rightsquigarrow \frac{\epsilon_0}{2\pi} \int_{-\infty}^{\infty} [\epsilon - 1]\, e^{i\omega(t'-t)}\, d\omega = \lim_{|\omega| \to \infty} \frac{\epsilon_0}{2\pi} \oint [\epsilon - 1]\, e^{i\omega(t'-t)}\, d\omega$$

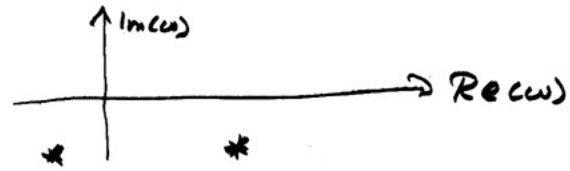
$$- \lim_{|\omega| \to \infty} \frac{i \cdot \epsilon_0}{2\pi} \int_0^{\pi} [\epsilon - 1]\, e^{i\omega(t'-t)} \cdot \omega\, e^{i\theta}\, d\theta$$

$\Rightarrow$

The second term vanishes because of the convergence of $[\varepsilon - 1]$ as ω^{-2}

$$\hookrightarrow \; G(t-t') = \lim_{|\omega| \to \infty} \frac{\varepsilon_0}{2\pi} \oint [\varepsilon - 1]\, e^{i\omega(t'-t)}\, d\omega \equiv 0$$

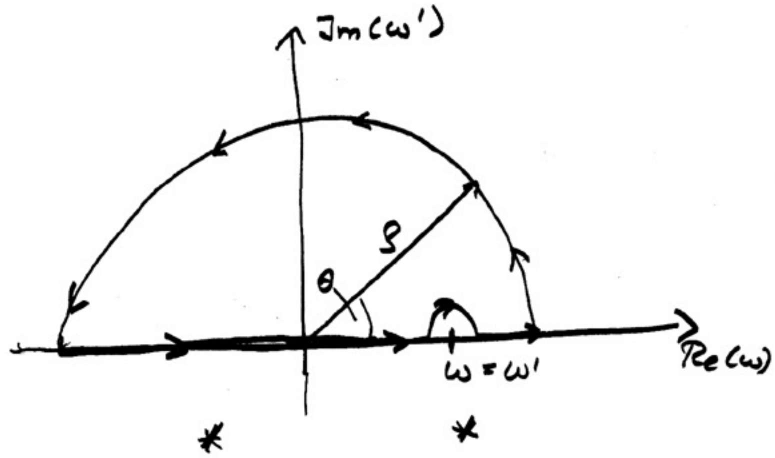
$\hookrightarrow$ By Cauchy's integral theorem, this means that $G(\tau) = G(t-t')$ is analytic in the upper half of the plane: i.e. poles of $\varepsilon(\omega)$ are restricted to the lower half plane!



Consider next the integral

$$J(\omega) = \oint \frac{d\omega\,[\varepsilon - 1]}{\omega' - \omega}$$

Integration over the path along the axis representing the real part of ω' avoiding the pole at $\omega = \omega'$ by a half circle and closing the path by a large half circle back!



$\Longrightarrow$

$$\rightsquigarrow \; J(\omega) = 0 = \lim_{\delta \to 0} \left[\int_{-\infty}^{\omega-\delta} \frac{d\omega'}{\omega'-\omega} [\varepsilon(\omega')-1] + \int_{\omega+\delta}^{\infty} \frac{d\omega'}{\omega'-\omega} [\varepsilon(\omega')-1] \right]$$

$$+ \lim_{\delta \to 0} \int_{\pi}^{0} \frac{i\, d\theta\, \delta\, e^{i\theta}}{\delta\, e^{i\theta}} [\varepsilon(\omega')-1]$$

Make use of the knowledge that the integral of the large half-circle of radius ρ vanishes in the limit $\rho \to \infty$ [because of the convergence of $[\varepsilon(\omega)-1]$ is faster than $1/\omega'$! $\left([\varepsilon - 1] \sim \frac{1}{\omega^2}\right)$]

The integral

$$\lim_{\delta \to 0} \int_{\pi}^{0} \frac{i\, d\theta\, \delta\, e^{i\theta}}{\delta\, e^{i\theta}} (\varepsilon(\omega)-1) = -i\pi [\varepsilon(\omega)-1]$$

$$\hookrightarrow \; -i\pi [\varepsilon(\omega)-1] = P \int_{-\infty}^{\infty} \frac{d\omega'}{\omega'-\omega} [\varepsilon(\omega')-1]$$

Cauchy Hauptwert := principle value

From this we get the relations

$$\boxed{\begin{aligned} \mathrm{Re}[\varepsilon(\omega)] - 1 &= \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{d\omega'}{\omega'-\omega} \cdot \mathrm{Im}[\varepsilon(\omega')] \\[2ex] \mathrm{Im}[\varepsilon(\omega)] &= -\frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{d\omega'}{\omega'-\omega} \cdot \left[\mathrm{Re}\{\varepsilon(\omega')\} - 1\right] \end{aligned}}$$

<u>denote</u> $\mathrm{Re}\{\varepsilon(\omega)\} = \varepsilon^{r}(\omega)$ and $\mathrm{Im}\{\varepsilon(\omega)\} = \varepsilon^{i}(\omega)$ $\Longrightarrow$

$$\leadsto \quad \varepsilon^r(\omega) - 1 = \frac{1}{\pi} P\int_{-\infty}^{\infty} \frac{\varepsilon^i(\omega')\, d\omega'}{\omega' - \omega}$$

$$= \frac{1}{\pi}\left[P\int_{-\infty}^{0} \frac{\varepsilon^i(\omega)\, d\omega'}{\omega'-\omega} + P\int_{0}^{\infty} \frac{\varepsilon^i(\omega')\, d\omega'}{\omega'-\omega}\right]$$

$$= \frac{1}{\pi}\left[P\int_{0}^{\infty} \frac{\varepsilon^i(-\omega')\, d(-\omega')}{-\omega'-\omega} + P\int_{0}^{\infty} \frac{\varepsilon^i(\omega')\, d\omega'}{\omega'-\omega}\right]$$

Note: use $\varepsilon^i(\omega) = -\varepsilon^i(-\omega)$

$$= \frac{1}{\pi}\left[P\int_{0}^{\infty} \underbrace{\left\{\frac{1}{\omega'+\omega} + \frac{1}{\omega'-\omega}\right\}}_{= \frac{2\omega'}{\omega'^2 - \omega^2}} \varepsilon^i(\omega')\, d\omega'\right]$$

$$= \frac{2}{\pi} P\int_{0}^{\infty} \frac{\omega'\, \varepsilon^i(\omega')\, d\omega'}{\omega'^2 - \omega^2}$$

$$\hookrightarrow \boxed{\varepsilon^r = 1 + \frac{2}{\pi}\int_{0}^{\infty} \frac{\omega'\, \varepsilon^i(\omega')\, d\omega'}{\omega'^2 - \omega^2}}$$

Similarly, we get with $\varepsilon^r(\omega) = \varepsilon^r(-\omega)$

$$\varepsilon^i(\omega) = -\frac{1}{\pi} P\int_{-\infty}^{\infty} \frac{[\varepsilon^r(\omega') - 1]}{\omega'-\omega}\, d\omega'$$

$$= \frac{-1}{\pi}\left[P\int_{-\infty}^{0} \frac{[\varepsilon^r(\omega') - 1]}{\omega'-\omega}\, d\omega' + P\int_{0}^{\infty} \frac{[\varepsilon^r - 1]}{\omega'-\omega}\, d\omega'\right]$$

$$= \frac{-1}{\pi}\left[P\int_{0}^{\infty} \underbrace{\left\{\frac{1}{\omega'+\omega} - \frac{1}{\omega'-\omega}\right\}}_{= \frac{-2\omega}{\omega'^2 - \omega^2}} [\varepsilon^r(\omega') - 1]\, d\omega'\right]$$

$$= -\frac{2\omega}{\pi} P\int_{0}^{\infty} \frac{[\varepsilon^r - 1]}{\omega'^2 - \omega^2}\, d\omega'$$

$$\hookrightarrow \boxed{\varepsilon^i(\omega) = -\frac{2\omega}{\pi} P\int_{0}^{\infty} \frac{[\varepsilon^r(\omega') - 1]}{\omega'^2 - \omega^2}\, d\omega'}$$

$\widehat{=}$ Kramers – Kronig relations

$\Longrightarrow$

Similarly, we can derivate the Kramers-Kronig relations for the complex refractive index $\hat{n} = n - ik$:

$$n(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\omega'}{\omega'^2 - \omega^2} k(\omega') \, d\omega'$$

$$k(\omega) = -\frac{2\omega}{\pi} P \int_0^\infty \frac{n(\omega') - 1}{\omega'^2 - \omega^2} \, d\omega'$$

and $$n(\omega) = 1 + \frac{c}{\pi} \int_0^\infty \frac{\alpha(\omega')}{\omega'^2 - \omega^2} \, d\omega'$$

If $\alpha(\omega)$ is known over all frequencies, $n(\omega)$ can be calculated for any ω - and consequently - also for $k(\omega)$ and the dielectric function $\varepsilon(\omega)$.

From the Kramers-Kronig relation for $\varepsilon(\omega)$ follows trivially a sum-rule for the static dielectric constant of materials: i.e.

$$\varepsilon_1(0) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\varepsilon_2(\omega')}{\omega'} \, d\omega'$$

$\rightsquigarrow$ largest contributions are made by optical transitions of low energy $\hbar\omega'$.

Quantum mechanical theory of dielectric function

External electrical field:

$$E(\vec{r},t) = -\nabla\phi(\vec{r},t) - \frac{\partial}{\partial t}\vec{A}(\vec{r},t)$$

ϕ - scalar potential
$\vec{A}$ - vector potential

is interacting with electronic charges of solid!

↳ perturbation of kinetic and potential energy, which modifies the SE (Schrödinger equation) - hamiltonian:

$$\boxed{H = \frac{1}{2m}\left\{\frac{\hbar}{i}\nabla + q\,\vec{A}(\vec{r},t)\right\}^2 + V(\vec{r}) - q\,\phi(\vec{r},t) = H_0 + H'}$$

a TEM wave can be represented in two alternative ways:

(1) $\phi(\vec{r},t) = \vec{E}(\vec{r},t)\cdot\vec{r} = \vec{E}_0\cdot\vec{r}\cdot\exp[i(\vec{k}_0\cdot\vec{r}-\omega t)] + c.c.$

↳ $\vec{A}(\vec{r},t) = 0$

(2) $A(\vec{r},t) = -\frac{ic}{\omega}\vec{E}_0\, e^{i(\vec{k}\vec{r}-\omega t)} + c.c.$

↳ $\phi(\vec{r},t) = 0$

In either case, the perturbation is small ⇝

1st-order perturbation theory is appropriate!

⟹

$\rightsquigarrow$ 1.) Scalar potential representation

$$\mathcal{H} = H_0 + H' \quad \text{with } H' = -q\phi(\vec{r},t) \,, \quad H_0 = \frac{1}{2m}\vec{p}^2 + V(\vec{r})$$

$$H' = -q\phi = -q\cdot(\vec{E}_0 \bullet \vec{r})\exp[i(\vec{k}\vec{r} - \omega t)] + c.c.$$

$$\hookrightarrow \quad \psi_Q(\vec{r},t) = |Q\rangle \cdot e^{-i\omega_Q t} + \psi^{(1)}(\vec{r},t) + \dots$$

$\rightsquigarrow$ Solve SE to calculate expectations of electric dipol operator

$$-q\langle Q'|\vec{r}|Q\rangle = \vec{r}_{QQ'}\cdot(-q)$$

$$= -q\int_V \psi_{Q'}^* \,\vec{r}\,\psi_Q \,d\tau$$

for all transitions between filled and empty states at single atomic center, to get

$$P(t) = -q\sum_{dQ}\vec{r}_{Q'Q} = \varepsilon_0(\varepsilon - 1)\vec{E}$$

$$\rightsquigarrow \boxed{\varepsilon(\omega) = 1 - \omega_p^2 \sum_{Q'Q} \frac{f_{Q'Q}}{\omega^2 - \omega_{QQ'}^2}}$$

with oscillator strength

$$f_{Q'Q} = \frac{2m\,E_{Q'Q}}{\hbar^2}\cdot|\vec{\xi}\bullet\vec{r}_{Q'Q}|$$

(compare to classical oscillator of mass m_0 and charge $-q$, for which $f_{Q'Q} = 1$) $\Rightarrow$

2.) Vector potential representation:

Extended states (sharply defined in momentum - but not in position) can be represented by vector potential $\vec{A}(\vec{r},t)$ formulation of source wave:

$$H = \frac{1}{2m}\left(\vec{p} - \frac{q}{c}A(\vec{r},t)\right)^2 + V(\vec{r}) = H_0 + H'$$

Use linear Taylor expansion and $\vec{A}^2 = 0$ to get

$$\boxed{H' = \frac{q}{mc}\ \vec{A}\cdot\vec{p}}$$

The transition propability for one e^- in the state k (@ time t) in the band $\vec{j}$ $\rightarrow$ into state k' (@ time t') in the band $\vec{j}'$

is $$W(j,j',k,\omega,t) = \frac{e^2 A_0^2}{m^2c^2}\,|M_{jj'}(k)|^2\, 2\pi\hbar\cdot t\ \delta(E_{j'}(k) - E_j(k) - \hbar\omega)$$

with the transition matrix element

$$M_{jj'}(k) = \langle j'k|\, H'\,|\, jk\rangle$$

To get the sum of all transitions per volume- and time unit, we integrate over the whole BZ and divide through the time t:

$$W(\omega) = \sum_{j,j'} \frac{1}{t}\,\frac{2}{(2\pi)^3}\cdot\int W(j,j',k,\omega,t)\, d\tau_k$$

$\Longrightarrow$

→ The probability that one photon $\hbar\omega$ will be absorbed within a given time unit can be related with the macroscopic defined imaginary part of $\varepsilon(\omega)$ through

$$\varepsilon_2 = \frac{4\pi c^2 \hbar}{\omega^2 A_0^2} \cdot \underbrace{W_a(\omega)}_{\substack{\text{energy loss} \\ \text{- macroscopic}}} = \underbrace{W(\omega)}_{\text{microscopic}}$$

$$\boxed{\varepsilon_2 = \frac{4\pi^2 e^2}{\hbar\omega} \sum_{j,j'} \frac{2}{(2\pi)^3} \int |M_{jj'}|^2 \, \delta(E_{j'}(k) - E_j(k) - \hbar\omega)\, d\tau_k}$$

transform the integral over BZ in an integral over an area of constant energy

$$\boxed{\varepsilon_2 = \alpha_x \sum_{jj'} \frac{2}{(2\pi)^3} \int_{E_{j'}-E_j=\hbar\omega} |M_{jj'}|^2 \frac{df}{|\nabla_k (E_{j'}(k) - E_j(k)|}}$$

with $\alpha_x = \dfrac{4\pi^2 e^2}{\hbar\omega}$

$$M_{jj'} = \langle \psi_{j'}(\vec{k}+\vec{q},\vec{r}) \,|\, e^{i\vec{q}\cdot\vec{r}}\; \vec{e}\cdot\vec{p} \,|\, \psi_j(\vec{k},\vec{r})\rangle$$

$\vec{e}$: unit vector in direction of EM-field

$\vec{p} = \frac{\hbar}{i}\nabla$ momentum