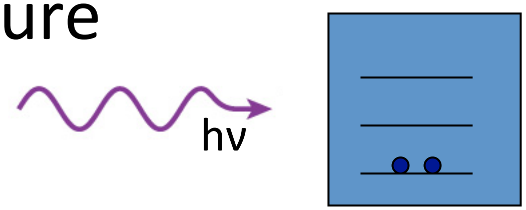
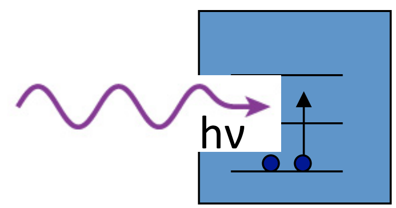
Light Interacts with Matter: Basic Process

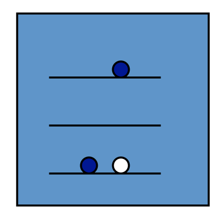
- Initial State
  - Photon + ground-state nanostructure

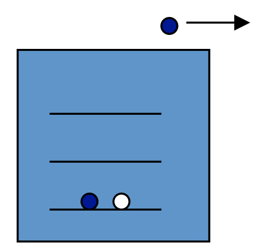


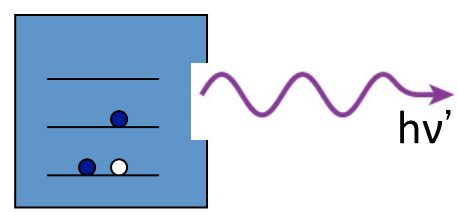
- Transition
  - Absorption event (~ 10^{-17} sec)



- Final State
  - Excited-state nanostructure
  - By products:
    - Absorption -- nothing
    - Photoemission -- emitted electron
    - Raman -- emitted photon

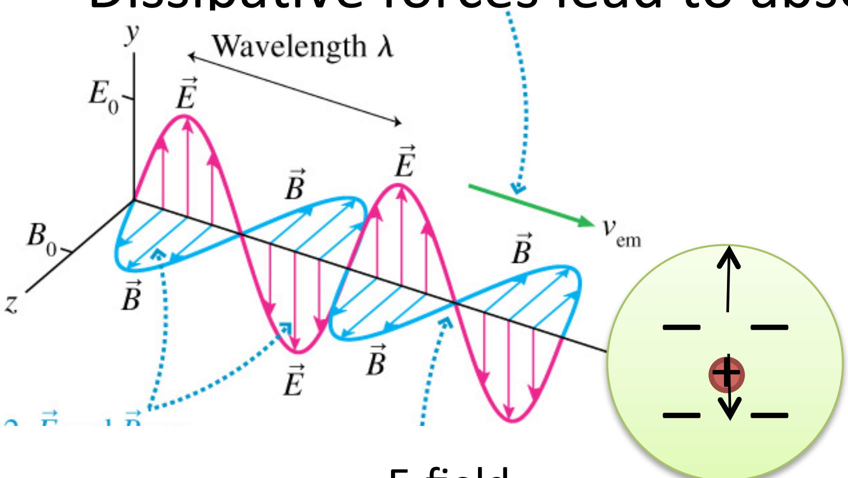






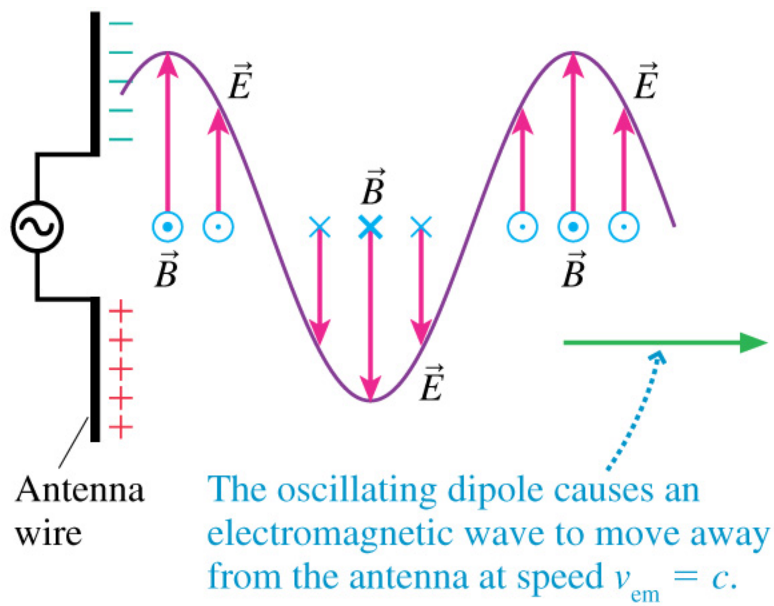
Basic Interaction in Classical Picture

- Electric field acts on charges
- Negative and positive charges separate, causing dipole moment
- Oscillating dipole radiates EM field
- This process slows down light propagation and change its phase
- Dissipative forces lead to absorption



E-field

Polarized
atom



Maxwell's Equations and Constituent Relations

Gauss' Law

$$\nabla \bullet \mathbf{D} = \rho \qquad \nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$$

Faraday's Law

$$\nabla \bullet \mathbf{B} = 0 \qquad \nabla \times \mathbf{H} = \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t}$$

Ampere's Law

Dielectric constant ε, Polarization Density **P** and Susceptibility χ:

$$\mathbf{D} = \varepsilon \varepsilon_o \mathbf{E} = \varepsilon_o \mathbf{E} + \mathbf{P} \quad \mathbf{P} = \chi \varepsilon_o \mathbf{E} = (\varepsilon - 1)\varepsilon_o \mathbf{E}$$

Permeability μ, Magnetization **M** and Magnetic Susceptibility χ_M:

$$\mathbf{B} = \mu \mu_o \mathbf{H} = \mu_o(\mathbf{H} + \mathbf{M}) \quad \mathbf{M} = \chi_M \mathbf{H} = (\mu - 1)\mathbf{H}$$

Conductivity σ (Ohm's Law) and Charge Conservation:

$$\mathbf{J} = \sigma \mathbf{E}; \quad \vec{\nabla} \bullet \vec{\mathbf{J}} + \frac{\partial \rho}{\partial t} = 0$$

EM Wave Solution

- Assume Plane Wave solution: $\mathbf{E} = \hat{\mathbf{e}}\ E_o\ e^{i(\mathbf{k}\bullet\mathbf{x}-\omega t)}$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}; \quad \nabla \times \mathbf{H} = \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t}$$

$$\Downarrow$$

$$i\mathbf{k} \times \mathbf{E} = i\omega\mu\mu_o\mathbf{H}$$

$$i\mathbf{k} \times \mathbf{H} = \sigma\mathbf{E} - i\omega\varepsilon\varepsilon_o\mathbf{E} = -i\omega(\varepsilon\varepsilon_o + i\sigma / \omega)\mathbf{E}$$

This has a solution for: $$k^2 = \omega^2\mu\mu_o\varepsilon_o\left(\varepsilon + i\frac{\sigma}{\omega\varepsilon_o}\right) = \mu\frac{\omega^2}{c^2}\hat{\varepsilon}$$

Complex dielectric function or complex conductivity?

- Real ε ~ Imaginary σ and vice versa
- Low ω: treat as σ, with Im(σ) = capacitive response
- High ω: treat as ε, with Im(ε) = absorption

Optical Constant Relationships
n, ε, and χ

- EM Wave:
  - Complex ε implies Complex wave vector

$$k=\frac{\omega}{c}\sqrt{\hat{\varepsilon}}\equiv\hat{n}\frac{\omega}{c}=k_{real}+ik_{imag}=k_o(n+i\kappa)$$

$$\vec{\mathbf{E}}=\hat{\mathbf{e}}\;E_o e^{i(kz-\omega t)}=\hat{\mathbf{e}}\;E_o e^{-i\omega t}e^{+ink_o z}e^{-\kappa k_o z}$$

Phase velocity

absorption

Dielectric constant ε, Susceptibility χ and Index of Refraction *n*:

$$\hat{\varepsilon}=\varepsilon_r+i\varepsilon_{im}=\varepsilon'+i\varepsilon''=\hat{n}^2=n^2-\kappa^2+2in\kappa$$

$$\hat{\chi}=\hat{\varepsilon}-1=\chi_r+i\chi_{im}=(\varepsilon_r-1)+i\varepsilon_{im}$$

Susceptibility is the true response function and satisfies KK-relation:

$$\chi_{im}(\omega)=-\frac{2\omega}{\pi}\wp\int_0^\infty\frac{\chi_r(\omega')}{\omega'^2-\omega^2}d\omega' \qquad \chi_r=+\frac{2}{\pi}\wp\int_0^\infty\frac{\omega'\chi_{im}(\omega')}{\omega'^2-\omega^2}d\omega'$$

Optical Constants Control Reflection, Transmission and Absorption

- Absorption (α) and Transmission (T)

$$E = E_o e^{-i\omega t} e^{+ink_o z} e^{-\kappa k_o z}$$

$$Intensity \propto |E|^2 = I_o e^{-2\kappa k z} = I_o e^{-\alpha_{opt} z}$$

Imaginary index of refraction

$$\alpha_{opt} = 2\kappa \frac{\omega}{c} = -\frac{1}{I}\frac{dI}{dz} = -\frac{d}{dz}\ln I = -\frac{1}{z}\ln\frac{I(z)}{I_o}$$

Note this is Incident - Reflected

$$\alpha_{opt} z = -\ln T(z)$$

Transmission

- Reflection
  - Depends on angle and polarization

$$r_s = \frac{n_1 \cos\theta_2 - n_2 \cos\theta_1}{n_1 \cos\theta_2 + n_2 \cos\theta_1} \qquad r_p = \frac{n_1 \cos\theta_1 - n_2 \cos\theta_2}{n_1 \cos\theta_1 + n_2 \cos\theta_2}$$

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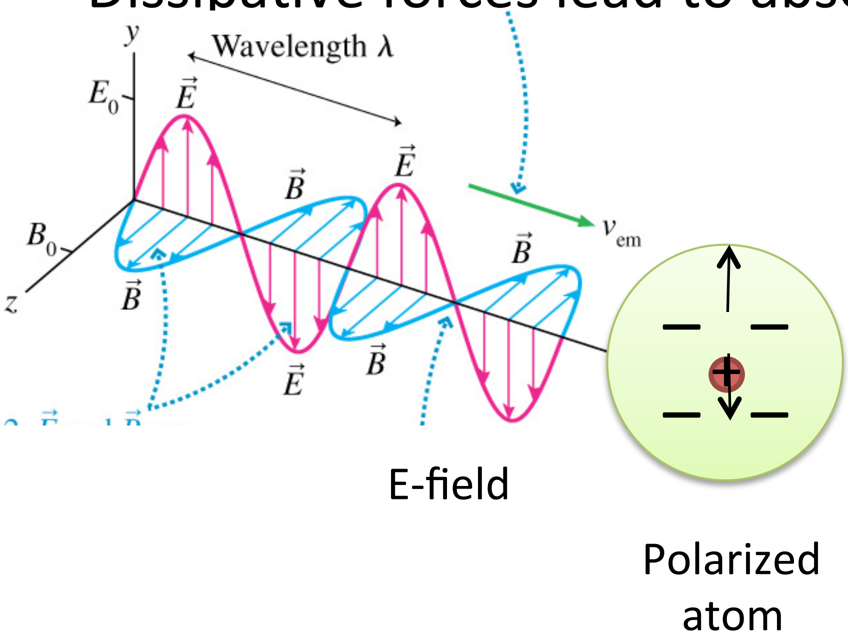
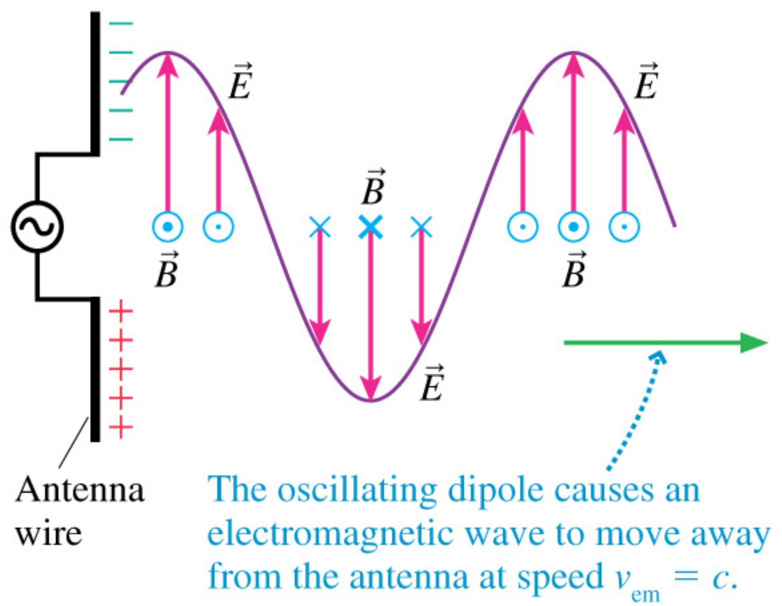




So what is the susceptibility?

- Response of internal charges of a medium to an applied electric field

$$\vec{\mathbf{P}} = \chi \varepsilon_o \vec{\mathbf{E}}$$

Various models:

1. Free electron gas
2. Free electron gas with damping
3. Bound electron gas with damping
4. Quantum mechanical excitations

$$\chi = -\frac{\omega_p^2}{\omega^2 - \omega_o^2 + i\omega\Gamma}$$

Momentum matrix element

Joint density of states

$$\chi_{im}(\omega) = \frac{2\hbar}{\varepsilon_o \omega^2} \frac{R_{c \leftarrow v}}{|A|^2} = \left(\frac{e}{2m\omega\varepsilon_o}\right)^2 |\wp_{cv}|^2 \sum_{\mathbf{k}} \delta(E_c(\mathbf{k}) - E_v(\mathbf{k}) - \hbar\omega)$$

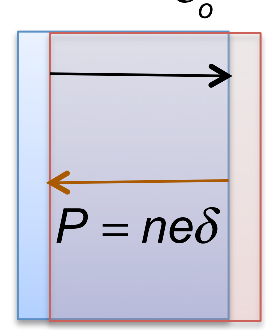
Classical Model 1 : Free Electron Gas

This the relevant model for the surface plasmon lab.

- Consider free electrons in a compensating fixed positive background.
- Release a static displacement of electrons δ:

$$F = ma = qE = -e * \frac{ne\delta}{\varepsilon_o}$$

$$E_{ind} = \frac{ne\delta}{\varepsilon_o}$$



+neδ -neδ

(n = volume density)

This has the form *F = -kx*, which is a harmonic oscillator with frequency

$$\omega_o = \sqrt{\frac{k}{m}}$$

This defines the **plasma frequency:** $\omega_p = \sqrt{\frac{ne^2}{m\varepsilon_o}}$

For Na density of 2.5 x 10^{22} cm^{-3}, $\hbar\omega_p$ ~ 9.2 eV; for doping at 10^{17} cm^{-3}, around 10 meV

EM Wave in a FEG

- Drive the system with E field at frequency ω:

$$E_{app} = E_o e^{-i\omega t}; \quad \delta = \delta_o e^{-i\omega t}$$

$$F = ma \Rightarrow -m\omega^2 \delta = -eE_{app}$$

$$\delta = \frac{e}{m\omega^2} E_{app}$$

- χ is the ratio of the Polarization Field to the Electric Field.
- **P** is the dipole moment per unit volume.
- For *n* charges per unit volume displaced by δ,

$$P = -ne\delta = -\frac{ne^2}{m\omega^2} E_{app} = -\frac{\omega_p^2}{\omega^2} \varepsilon_o E_{app}$$

$$P = \chi \varepsilon_o E_{app}$$

$$\chi = -\frac{\omega_p^2}{\omega^2}; \quad \varepsilon_{FEG} = 1 - \frac{\omega_p^2}{\omega^2}$$

FEG Dielectric Function

If $\omega < \omega_p : \varepsilon_{FEG} < 0 \Rightarrow$ *imaginary index*

absorption and high reflectivity

Classical Model 2: FEG with damping

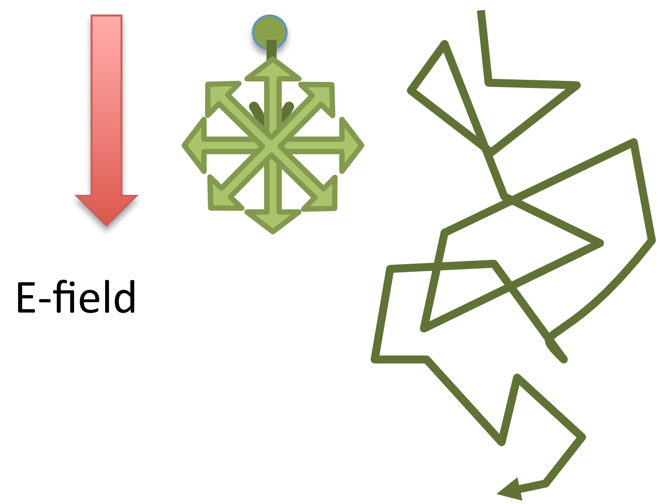
This the relevant model for the Hall effect lab

- Response to <u>**DC field**</u>: standard conductivity
  - Electron accelerates in E-field until it scatters after a time τ
  - That scattering event makes the average momentum *p* in the drift direction zero, since it sends the particle into an arbitrary direction.

$$F = ma = \frac{dp}{dt} = qE - \frac{p}{\tau}$$

Steady state solution: $p = qE\tau = mv$

Define mobility: $v = \mu E = \frac{e\tau}{m}$



And DC conductivity: $J = \sigma E$

$$nev = \sigma E$$

$$\sigma = ne\mu = \frac{ne^2\tau}{m} = \omega_p^2 \tau \varepsilon_o$$

Frequency response of damped FEG

- Same equation – finite frequency
  - Usually replace $\tau = 1/\Gamma$ – damping instead of scattering.
  - Whether think in terms of conductivity with some capacitive response or dielectric with some absorption depends on $\omega\tau$.

$$F = ma = \frac{dp}{dt} = qE - \frac{p}{\tau} = -eE - mv\Gamma$$ Steady state response: $$x = \frac{e/m}{\omega^2 + i\omega\Gamma} E_{app}$$

Complex x means response not in phase with applied field.

Solve for real and imaginary susceptibility, $\chi = -nex$:

$$\chi = -\frac{\omega_p^2}{\omega^2 + i\omega\Gamma} = -\frac{\omega_p^2}{\omega^2 + \Gamma^2} + i\frac{\sigma_o}{\omega\varepsilon_o}\frac{\Gamma^2}{\Gamma^2 + \omega^2}$$

$$= \chi_{FEG}\frac{1}{1+(\omega\tau)^{-2}} + i\frac{\sigma_o}{\omega\varepsilon_o}\frac{1}{1+(\omega\tau)^2}$$

Dominate for $\omega\tau \gg 1$ (first term)

Dominate for $\omega\tau \ll 1$ (second term)

Classical Model 3: Bound electron gas

This the relevant model for optical absorption, which isn't in any current Phys 431 labs.

- Add a restoring force with resonant frequency ω_o.
  - We'll see later this is equivalent to an absorption at $\hbar\omega_o$.

Force equation:

$$F = ma = -eE_{app} - m\Gamma v - m\omega_o^2 x$$

Response:

$$x = \frac{eE/m}{\omega^2 - \omega_o^2 + i\omega\Gamma}$$

Susceptibility:

$$\chi_{osc} = -f_j \frac{\omega_p^2}{\omega^2 - \omega_j^2 - i\omega\Gamma_j}$$

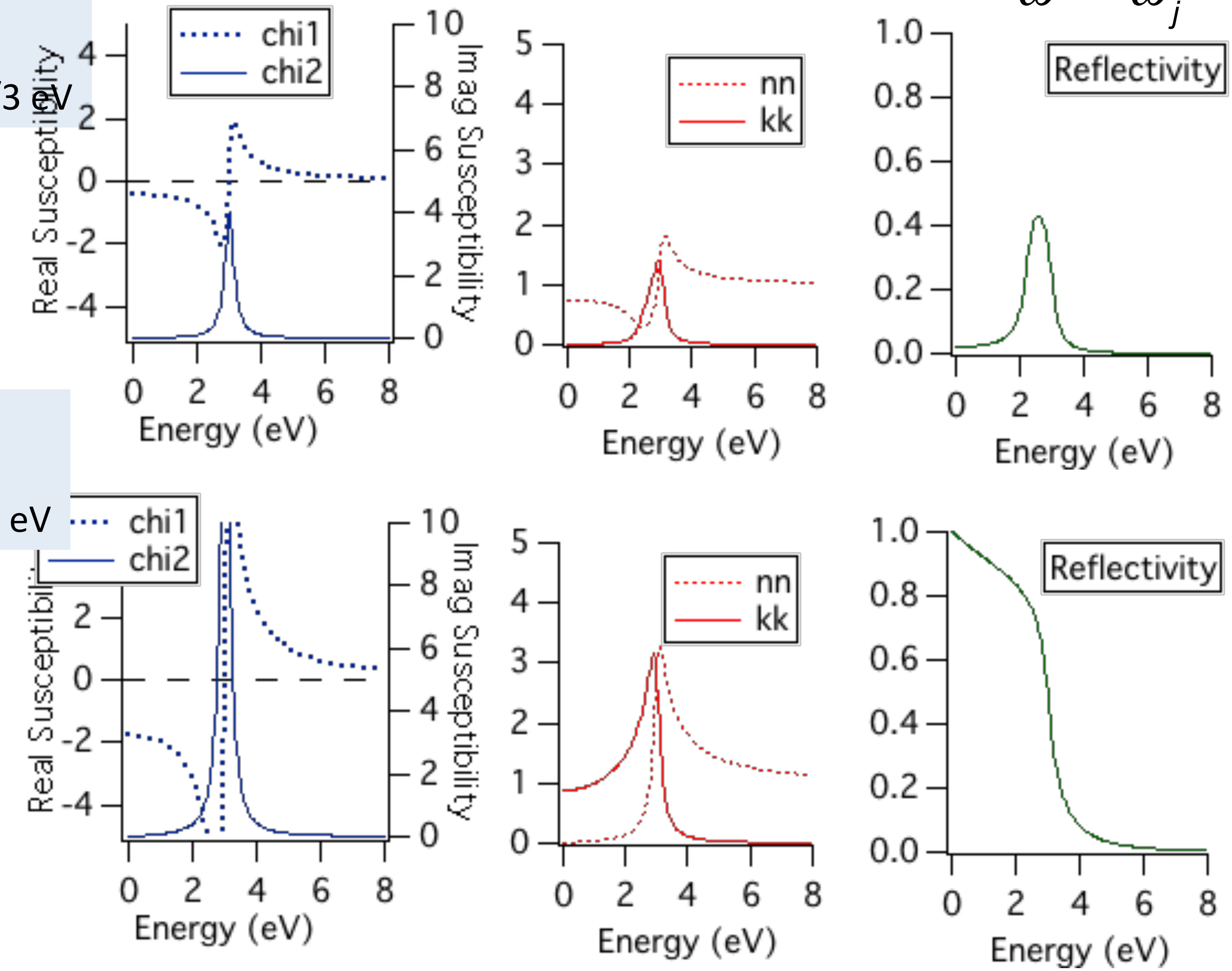
f is the **oscillator strength**, effectively the fraction of the electron density participating in this resonance.

Example of Bound EG response

$$\chi_{osc} = -f_j \frac{\omega_p^2}{\omega^2 - \omega_j^2 - i\omega\Gamma_j}$$

Wp = 2 eV
Wo = 3 eV
Gamma = 1/3 eV

Wp = 4 eV
Wo = 3 eV
Gamma = 1/3 eV



All well and good, but what about quantum mechanics??

The remaining slides were created for another purpose, and are just here for your enlightenment.

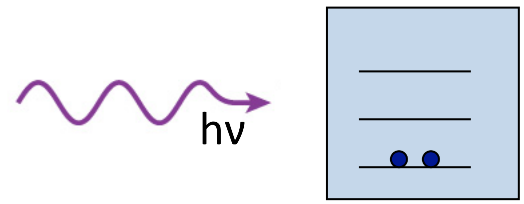
They will make more sense if you have taken E&M and QM.

We don’t have any labs in Phys 431 that require the quantum mechanical picture of the dielectric constant.

All well and good, but what about quantum mechanics??

Connection is through the Absorption Coefficient

- Macroscopic wave propagation is classical
- Photon absorption is a quantum event.



Absorption Coefficient: $I = I_o e^{-\alpha z} = I_o e^{-2\kappa\omega z/c}$

- Quantum mechanics gives rates wrt time, not position

$$-\frac{dI}{dt} = -\frac{dI}{dz}\frac{dz}{dt} = (\alpha I)\left(\frac{c}{n}\right) = \frac{\varepsilon''\omega}{n^2} I$$

Real part of index

$$I = \frac{cn^2\varepsilon_o}{2}\left|E(\omega)\right|^2 = \frac{cn^2\varepsilon_o}{2}\left|\omega A\right|^2 = \frac{n^2\omega^2 c\varepsilon_o}{2}|A|^2$$

Imaginary part of ε

A = vector potential in Coulomb gauge

$$\frac{\text{energy absorbed}}{\text{time}} = \frac{\varepsilon''\omega^3\varepsilon_o}{2}|A|^2$$

Quantum Description: Fermi Golden Rule

$$\frac{\textit{energy absorbed}}{\textit{time}} = R_{c\leftarrow v}\hbar\omega$$

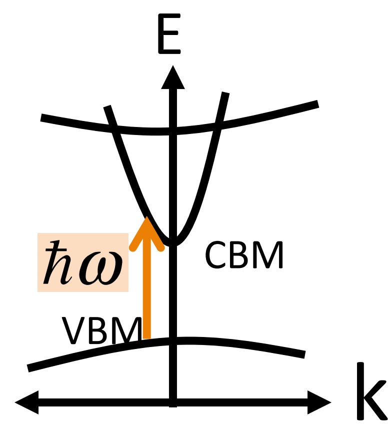
$$R_{c\leftarrow v} = \frac{2\pi}{\hbar}\sum_{\mathbf{k}_c,\mathbf{k}_v}\underbrace{\left|\left\langle c\left|H_{e-Rad}\right|v\right\rangle\right|^2}_{\text{Matrix element}}\underbrace{\delta(E_c(\mathbf{k}_c)-E_v(\mathbf{k}_v)-\hbar\omega)}_{\text{Joint density of states}}$$

Matrix element — Symmetry

Joint density of states

$$\frac{\textit{energy absorbed}}{\textit{time}} = \frac{\varepsilon''\omega^3\varepsilon_o}{2}|A|^2$$

$$\varepsilon''(\omega) = \chi''(\omega) = \frac{2\hbar}{\varepsilon_o\omega^2}\frac{R_{c\leftarrow v}}{|A|^2}$$



This is why χ is more fundamental than the index of refraction or absorption coefficient.

You can use KK-relation to get the real part.

What is the Hamiltonian?

- Potential Energy in electric field:

$$U = qV = -q\vec{\mathbf{E}} \bullet \vec{\mathbf{r}}$$

- Atom: **r** << λ and can ignore high order terms

$$\vec{\mathbf{E}} = \mathbf{E}_o e^{i\vec{\mathbf{k}} \bullet \vec{\mathbf{r}}} = \vec{\mathbf{E}}_o \left[1 + i\vec{\mathbf{k}} \bullet \vec{\mathbf{r}} - (\vec{\mathbf{k}} \bullet \vec{\mathbf{r}})^2 + \ldots \right]$$

- Crystal: **wave vector** is what is confined to small range, and not position
  - Use vector potential form of Hamiltonian

$$H_{e-r} = -q\vec{\mathbf{E}} \bullet \vec{\mathbf{r}} \quad vs. \quad H_{e-r} = \frac{e}{m} \vec{\mathbf{A}} \bullet \vec{\mathbf{p}}$$

Include EM field by changing momentum to **p** + *e***A**

Calculating the Matrix Element for Direct Gap Semiconductor

Coulomb gauge

$$\mathbf{E} = -\frac{\partial \mathbf{A}}{\partial t}; \quad \mathbf{B} = \nabla \times \mathbf{A}$$

$$\mathbf{A} = -\frac{1}{\omega}\mathbf{E}_o \cos(\mathbf{q} \bullet \mathbf{r} - \omega t) = \frac{-1}{2\omega}\mathbf{E}_o \left(e^{i(\mathbf{q} \bullet r - \omega t)} + e^{-i(\mathbf{q} \bullet \mathbf{r} - \omega t)} \right)$$

Hamiltonian

$$H = \frac{(\mathbf{p} + e\mathbf{A})^2}{2m} + V(\mathbf{r})$$

$$= \frac{p^2}{2m} + \frac{e}{2m}\mathbf{p} \bullet \mathbf{A} + \frac{e}{2m}\mathbf{A} \bullet \mathbf{p} + \frac{e^2 A^2}{2m} + V(\mathbf{r})$$

Matrix Element

$$\left| \langle c | H_{e-Rad} | v \rangle \right|^2 = \left(\frac{e}{m} \right)^2 \left| \langle c | A_x p_x + A_y p_y + A_z p_z | v \rangle \right|^2$$

$$|c\rangle = u_c e^{i\mathbf{k}_c \bullet \mathbf{r}}; \; |v\rangle = u_v e^{i\mathbf{k}_v \bullet \mathbf{r}} \qquad p_x u_v e^{i\mathbf{k}_v \bullet \mathbf{r}} = \underline{e^{i\mathbf{k}_v \bullet \mathbf{r}} p_x u_v} + \underline{\hbar k_v u_v e^{i\mathbf{k}_v \bullet \mathbf{r}}}$$

Important term

Integrates to zero u_v orthog. to u_c

More matrix element

$$\int_{crystal} u^*_c \, e^{+i(\mathbf{q}+\mathbf{k}_v-\mathbf{k}_c)\bullet\mathbf{r}} p_x u_v d^3r =$$

$$= \sum_{j=\text{lattice pnts}} e^{+i(\mathbf{q}+\mathbf{k}_v-\mathbf{k}_c)\bullet\mathbf{R}_j} \int_{\text{unit cell}} u^*_c \, e^{+i(\mathbf{q}+\mathbf{k}_v-\mathbf{k}_c)\bullet\mathbf{r}'} p_x u_v d^3r'$$

$$e^{i(\mathbf{q}\bullet\mathbf{r}')} = 1 \; (+i\mathbf{q}\bullet\mathbf{r}' + \frac{1}{2}(i\mathbf{q}\bullet\mathbf{r}')^2 + \ldots)$$

Electric quadrupole

Magnetic dipole

Main term

Momentum conservation:

$$\mathbf{q}+\mathbf{k}_v-\mathbf{k}_c = 0 \quad or \quad \mathbf{G}$$

$$\left| \int_{\text{unit cell}} u^*_c \, p_x u_v d^3r' \right|^2 = \frac{1}{3} |\wp|^2$$

Net result:

$$\left|\langle c | H_{e-Rad} | v \rangle\right|^2 = \left(\frac{e}{2m}\right)^2 |A|^2 |\wp_{cv}|^2$$

Momentum matrix element
Between valence and conduction bands

Pull together and connection to ε

$$R_{c\leftarrow v} = \frac{2\pi}{\hbar}\sum_{\mathbf{k}_c,\mathbf{k}_v}\left|\langle c|H_{e-Rad}|v\rangle\right|^2 \delta(E_c(\mathbf{k}_c)-E_v(\mathbf{k}_v)-\hbar\omega)$$

$$= \frac{2\pi}{\hbar}\left(\frac{e}{2m}\right)^2 \left|A(\omega)\right|^2 \left|\wp_{cv}\right|^2 \sum_{\mathbf{k}}\delta(E_c(\mathbf{k}+\mathbf{q})-E_v(\mathbf{k})-\hbar\omega)$$

$$\varepsilon''(\omega) = \frac{2\hbar}{\varepsilon_o\omega^2}\frac{R_{c\leftarrow v}}{|A|^2} = \left(\frac{e}{2m\omega\varepsilon_o}\right)^2 \left|\wp_{cv}\right|^2 \sum_{\mathbf{k}}\delta(E_c(\mathbf{k})-E_v(\mathbf{k})-\hbar\omega)$$

Joint density of states

Kramers-Kronig:

$$\varepsilon' = 1+\frac{2}{\pi}\int\frac{\omega'}{\omega'^2-\omega^2}\left(\frac{e}{2m\varepsilon_o\omega'}\right)^2 \left|\wp_{cv}\right|^2 \sum_{\mathbf{k}}\frac{\delta(\omega_{cv}-\omega')}{\hbar}d\omega'$$

$$\varepsilon' = 1+\frac{e^2}{\varepsilon_o m}\left[\sum_{\mathbf{k}}\frac{1}{2\pi m\hbar\omega_{cv}}\left|\wp_{cv}\right|^2\frac{1}{\omega_{cv}^2-\omega^2}\right]$$

Bound electron gas

$$\varepsilon_{BEG}(\omega) = 1-\frac{\omega_p^2}{\omega^2-\omega_o^2}$$

$$\varepsilon' = 1-\sum_{\mathbf{k}}\frac{\frac{f_i(\mathbf{k})e^2}{m\varepsilon_o}}{\omega^2-\omega_{cv}^2}$$

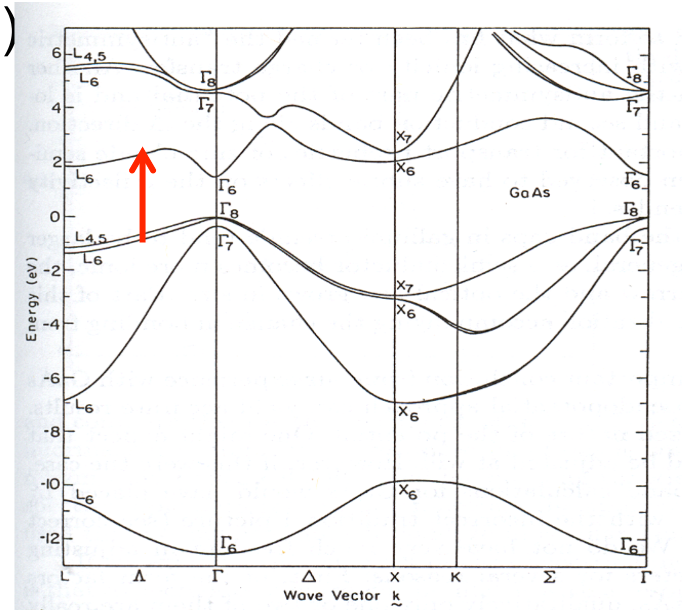
Oscillator strength ~
Matrix element

$$f_{cv}(\mathbf{k}) = \frac{1}{2\pi m\hbar\omega_{cv}}\left|\wp_{cv}\right|^2$$

Transition frequency

Joint Density of States

$$\varepsilon''(\omega) = \left(\frac{e}{2m\varepsilon_o\omega}\right)^2 \left|\wp_{cv}\right|^2 \sum_{\mathbf{k}} \delta(E_c(\mathbf{k}) - E_v(\mathbf{k}) - \hbar\omega)$$



Sum over occupied *v* and empty *c* states with same **k** separated by $\hbar\omega$

$$3D: \ \rho_j(E_{cv}) = \frac{2}{(2\pi)^3} \int \frac{dS_k}{\left|\nabla_k(E_{cv})\right|}$$

Critical point: denominator goes to zero

$$E_{cv}(\mathbf{k}) = E_o(\mathbf{k}_o) + [linear = 0] + \sum_{i=1}^{\dim} \alpha_i (\mathbf{k} - \mathbf{k}_o)_i^2$$

Critical points

$$E_{cv}\left(\mathbf{k}\right) = E_o(\mathbf{k}_o) + \sum_{i=1}^{\dim} \alpha_i \left(\mathbf{k} - \mathbf{k}_o\right)_i^2$$

Subscript = number of negative α’ s

Shape of curve gives info on dimensionality and band structure

Dimension	*Type*	$D_j(E<E_o)$	$D_j(E<E_o)$
3	M_0	0	$\sqrt{E-E_o}$
	M_1	$C-\sqrt{E_o-E}$	C
	M_2	C	$C-\sqrt{E-E_o}$
	M_3	$\sqrt{E_o-E}$	0