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Optical Spectroscopy in Materials Science
Response functions from quantum mechanics

Interaction between light and matter in quantum mechanics

Semi-classical approach in linear optics:

- electrons are described by quantum mechanics
- electromagnetic field is classical (not quantized)

$$H = \frac{(p - eA)^2}{2m} + V + e\phi$$

$$H_0 = \frac{p^2}{2m} + V$$

$$H_{\text{int}} \approx \frac{e(pA + Ap)}{2m} + e\phi$$

Electromagnetic potentials:

$$E = -\nabla\phi - \frac{\partial A}{\partial t}$$

$$B = \nabla \times A$$

Gauge freedom $A' = A + \nabla\Lambda$

$$\phi' = \phi - \frac{\partial \Lambda}{\partial t}$$

Following equations are satisfied by definition:

$$\nabla \cdot \mathrm{B} = 0$$

$$\nabla \times \mathrm{E} = -\partial_t \mathrm{B}$$

The other two equations:

$$\nabla \cdot \mathrm{E} = \frac{1}{\varepsilon_0}\rho$$

$$\nabla \times \mathrm{B} = \mu_0(\mathrm{j} + \varepsilon_0 \partial_t \mathrm{E})$$

$$-\nabla^2\phi - \partial_t(\nabla \cdot \mathrm{A}) = \frac{1}{\varepsilon_0}\rho$$

$$\nabla(\nabla \cdot \mathrm{A}) - \nabla^2 \mathrm{A} = \mu_0 \mathrm{j}$$

Dynamic potentials in the long wavelength limit

In the long wavelength limit, λ>>a:

$$E_\nu(\underline{x}) = E_\nu(\underline{0}) + (\partial_\mu E_\nu)\big|_0 x_\mu + \dots$$

$$B_\nu(\underline{x}) = B_\nu(\underline{0}) + (\partial_\mu B_\nu)\big|_0 x_\mu + \dots$$

Statment 1.: The following expansion of the potentials describes the fields in the long wavelength limit

$$\phi(\underline{x}) = \phi(\underline{0}) - x_\alpha E_\alpha(\underline{0}) - \frac{1}{2} x_\alpha x_\beta (\partial_\beta E_\alpha)\big|_{\underline{0}} + \dots$$

$$A_\alpha(\underline{x}) = \frac{1}{2}\varepsilon_{\alpha\beta\gamma} B_\beta(\underline{0}) x_\gamma + \frac{1}{3}\varepsilon_{\alpha\gamma\delta} x_\beta (\partial_\beta B_\gamma)\big|_{\underline{0}} x_\delta + \dots$$

Proof:

$$E_\nu = -\partial_\nu \phi - \partial_t A_\nu$$

$$= -\partial_\nu \phi(\underline{0}) + (\partial_\nu x_\alpha) E_\alpha(\underline{0}) + \frac{1}{2}\partial_\nu(x_\alpha x_\beta)(\partial_\beta E_\alpha)\big|_{\underline{0}} - \partial_t \frac{1}{2}\varepsilon_{\nu\beta\gamma} B_\beta(\underline{0}) x_\gamma$$

$$= 0 + \delta_{\nu\alpha} E_\alpha(\underline{0}) + \frac{1}{2}(\delta_{\nu\alpha} x_\beta + \delta_{\nu\beta} x_\alpha)(\partial_\beta E_\alpha)\big|_{\underline{0}} + \frac{1}{2}\varepsilon_{\nu\beta\gamma} \underbrace{[-\partial_t B_\beta(\underline{0})]}_{\varepsilon_{\beta\alpha\mu}(\partial_\alpha E_\mu)|_0} x_\gamma$$

as $\nabla \times \underline{E} = -\partial_t \underline{B}$

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Proof:

$$E_\nu(\underline{x}) = E_\alpha(0) + \frac{1}{2}\left(x_\beta (\partial_\beta E_\nu)\big|_0 + x_\alpha (\partial_\nu E_\alpha)\big|_0\right) + \frac{1}{2}\left(\delta_{\alpha\gamma}\delta_{\nu\mu} - \delta_{\gamma\mu}\delta_{\nu\alpha}\right)(\partial_\alpha E_\mu)\big|_0 x_\gamma$$

$$= E_\nu(0) + \frac{1}{2}\left((\partial_\beta E_\nu)\big|_0 x_\beta + (\partial_\nu E_\alpha)\big|_0 x_\alpha\right) + \frac{1}{2}\left((\partial_\gamma E_\nu)\big|_0 x_\gamma - (\partial_\nu E_\mu)\big|_0 x_\mu\right)$$

$$= E_\nu(0) + (\partial_\beta E_\nu)\big|_0 x_\beta$$

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Proof:

$$B_\nu(\underline{x}) = \varepsilon_{\nu\mu\alpha} \partial_\mu A_\alpha(\underline{x}) = \varepsilon_{\nu\mu\alpha} \partial_\mu \left(\frac{1}{2} \varepsilon_{\alpha\beta\gamma} B_\beta(0) x_\gamma + \frac{1}{3} \varepsilon_{\alpha\gamma\delta} x_\beta (\partial_\beta B_\gamma)\big|_0 x_\delta \right)$$

$$= \frac{1}{2} \varepsilon_{\nu\mu\alpha} \varepsilon_{\alpha\beta\gamma} B_\beta(0) \delta_{\mu\gamma} + \frac{1}{3} \varepsilon_{\nu\mu\alpha} \varepsilon_{\alpha\gamma\delta} (\partial_\beta B_\gamma)\big|_0 (\delta_{\mu\beta} x_\delta + \delta_{\mu\delta} x_\beta)$$

$$= \frac{1}{2} \varepsilon_{\nu\mu\alpha} \varepsilon_{\beta\mu\alpha} B_\beta(0) + \frac{1}{3} \varepsilon_{\nu\beta\alpha} \varepsilon_{\gamma\delta\alpha} (\partial_\beta B_\gamma)\big|_0 x_\delta + \frac{1}{3} \varepsilon_{\nu\mu\alpha} \varepsilon_{\gamma\mu\alpha} (\partial_\beta B_\gamma)\big|_0 x_\beta$$

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Proof:

note: $\sum_{\alpha\beta\mu} \varepsilon_{\nu\mu\alpha}\varepsilon_{\beta\mu\alpha} = 2\sum_\beta \delta_{\nu\beta}$

$$= \frac{1}{2} 2\,\delta_{\nu\beta} B_\beta(0) + \frac{1}{3}(\delta_{\nu\gamma}\delta_{\beta\delta} - \delta_{\nu\delta}\delta_{\beta\gamma})(\partial_\beta B_\gamma)|_0 x_\delta + \frac{1}{3} 2\,\delta_{\nu\gamma}(\partial_\beta B_\gamma)|_0 x_\beta$$

$$= B_\nu(0) + \frac{1}{3}(\partial_\beta B_\nu)|_0 x_\beta - \frac{1}{3}(\partial_\beta B_\beta)|_0 x_\nu + \frac{2}{3}(\partial_\beta B_\nu)|_0 x_\beta$$

$$= B_\nu(0) + (\partial_\beta B_\nu)|_0 x_\beta$$

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$$B_\nu(x) = B_\nu(0) + (\partial_\mu B_\nu)\big|_0 x_\mu + \dots$$

$$\phi(x) = \phi(0) - x_\alpha E_\alpha(0) - \frac{1}{2} x_\alpha x_\beta (\partial_\beta E_\alpha)\big|_0 + \dots$$

$$A_\alpha(x) = \frac{1}{2}\varepsilon_{\alpha\beta\gamma} B_\beta(0) x_\gamma + \frac{1}{3}\varepsilon_{\alpha\gamma\delta} x_\beta (\partial_\beta B_\gamma)\big|_0 x_\delta + \dots$$

Statment 2.: This expansion satisfies $\nabla \cdot A = 0$ (Coulomb gauge)

Proof:

$$\partial_\alpha A_\alpha = \frac{1}{2}\varepsilon_{\alpha\beta\gamma} B_\beta(0)\, \partial_\alpha x_\gamma = \frac{1}{2}\varepsilon_{\alpha\beta\gamma} B_\beta(0) \cdot \delta_{\alpha\gamma} = 0$$

anti-symmetric ($\varepsilon_{\alpha\beta\gamma}$)   symmetric ($\delta_{\alpha\gamma}$)

In the Coulomb gauge $[p, A] = 0$

Ligth-matter interaction in the long wavelength limit

Using the expansion: $\phi(x) = \phi(0) - x_\alpha E_\alpha(0) - \frac{1}{2} x_\alpha x_\beta (\partial_\beta E_\alpha)|_0 + \dots$

$$A_\alpha(x) = \frac{1}{2}\varepsilon_{\alpha\beta\gamma} B_\beta(0) x_\gamma + \frac{1}{3}\varepsilon_{\alpha\gamma\delta}\, x_\beta (\partial_\beta B_\gamma)|_0\, x_\delta + \dots$$

$$\mathcal{H}_{int} = -\frac{e}{2m}(\underline{p}\cdot\underline{A} + \underline{A}\cdot\underline{p}) + e\phi - g\mu_B\, \underline{s}\cdot\underline{B}$$

(Zeeman term is included)

$$= -\frac{e}{2m}\varepsilon_{\alpha\beta\gamma} B_\beta(0) x_\gamma p_\alpha + e\left(\phi(0) - x_\alpha E_\alpha(0) - \frac{1}{2} x_\alpha x_\beta (\partial_\beta E_\alpha)|_0\right) - g\mu_B\, s_\alpha B_\alpha(0)$$

far from charges generating the field: $(\partial_\beta E_\beta)|_0 = 0$

$$= e\phi(0) - e x_\alpha E_\alpha(0) - \frac{1}{3}\left[\frac{e}{2}\left(3x_\alpha x_\beta - (x)^2 \delta_{\alpha\beta}\right)\right](\partial_\alpha E_\beta)|_0 - \frac{e\hbar}{2m}\left(L_\alpha/\hbar + g\, S_\alpha/\hbar\right) B_\alpha(0)$$

$$\mathcal{H}_{int} = -\mu_\alpha E_\alpha(0) - \frac{1}{3}\theta_{\alpha\beta}(\partial_\alpha E_\beta)|_0 - m_\alpha B_\alpha(0)$$

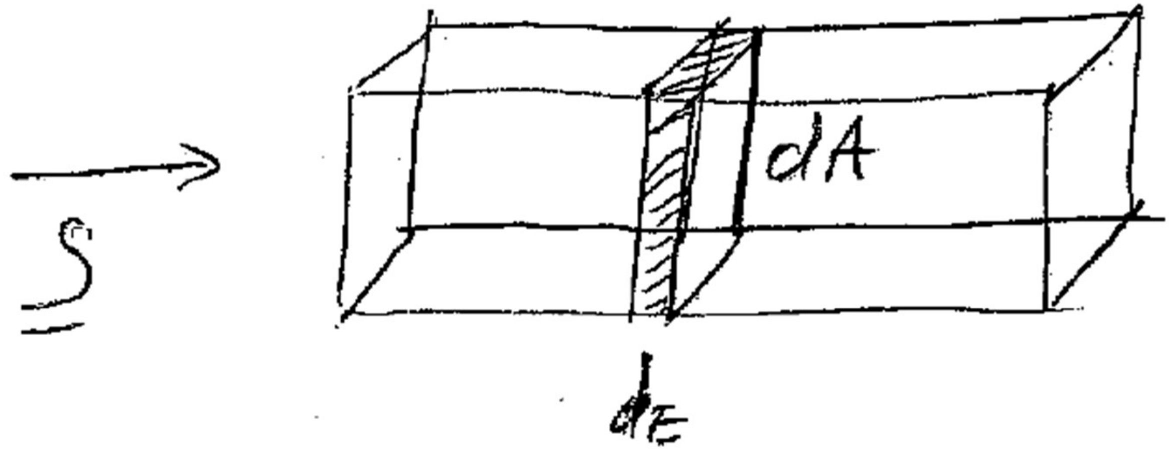
E1 – electric dipole   E2 – electric quadrupole   M1 – magnetic dipole

Absorption from time-dependent perturbation theory

$$\underline{S} = \underline{E}\times\underline{H} = \frac{q}{\omega\mu_0}E_0^2$$

$$\frac{dI}{dz} = -\alpha I$$

$$I\,\alpha\,dz = \frac{W_{n\to m}}{dA}\cdot\hbar\omega$$



Power loss in unit volume: dI/dz

$$\alpha = \frac{\frac{W_{n\to m}}{dA\,dz}\cdot\hbar\omega}{I} = \frac{2\pi\mu_0 c}{V\,n}\cdot\frac{\omega}{E^2}\left|\langle m|H_{int}|n\rangle\right|^2\delta(E_m-E_n-\hbar\omega)$$

Fermi's golden rule:

$$W_{n\to m} = \frac{2\pi}{\hbar}\left|\langle m|H_{int}|n\rangle\right|^2\delta(E_m-E_n-\hbar\omega)$$

Order of magnitude estimate of the multipole terms

Electric dipole excitations are usually far stronger:

$$\frac{\alpha_{E1}}{\alpha_{M1}} \sim \frac{(ea\cdot E)^2}{(\mu_B\cdot B)^2} \simeq \left(\frac{ea\cdot E}{\frac{e\hbar}{m}\cdot E/c}\right)^2 = \left(\frac{c}{\frac{\hbar/a}{m}}\right)^2 = \left(\frac{c}{v}\right)^2 \sim 10^4 .. 10^5$$

$$\frac{\alpha_{E1}}{\alpha_{E2}} \sim \frac{(ea\cdot E)^2}{(ea^2\cdot qE)^2} \sim \left(\frac{\lambda}{a}\right)^2 \sim 10^4$$

a – typical length scale of the electron could
v – typical velocity of the electrons
μ_B – Bohr magneton

$$v \approx \frac{\hbar}{ma}$$

Optical response functions from Kubo formula

When the system is driven by a perturbation $\mathcal{H}_{int} = -\hat{A} \cdot f(t)$

the response can be calculated $\langle \delta B(t) \rangle = \int \chi_{BA}(t-t') f(t') dt'$

Kubo formula: $\chi_{BA}(\tau) = \frac{i}{\hbar} \theta(\tau) \langle [B(\tau), A(0)] \rangle_0$

- works for a general (even interacting) system
- close to equilibrium: reponse comes from an expectation value calculated in equilibrium

$$\chi_{BA}(t) = \frac{i}{\hbar} \theta(t) \sum_n \langle n | \frac{e^{-\beta \mathcal{H}}}{Z} \left(e^{\frac{i}{\hbar} \mathcal{H} t} B e^{-\frac{i}{\hbar} \mathcal{H} t} A - A e^{\frac{i}{\hbar} \mathcal{H} t} B e^{-\frac{i}{\hbar} \mathcal{H} t} \right) | n \rangle$$

$$\sum_n |m\rangle\langle m| \qquad \sum_n |m\rangle\langle m|$$

$$\hbar \omega_{mn} = E_m - E_n$$

$$\chi_{BA}(t) = \frac{i}{\hbar} \theta(t) \sum_{n,m} \frac{e^{-\beta E_n} - e^{-\beta E_m}}{Z} e^{-i\omega_{mn} t} \langle n | B | m \rangle \langle m | A | n \rangle$$

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- works for a general (even interacting) system
- close to equilibrium: reponse comes from an expectation value calculated in equilibrium

Spectral decomposition:

$$\chi_{BA}(\omega) = -\frac{1}{\hbar} \sum_{n,m} \frac{e^{-\beta E_n} - e^{-\beta E_m}}{Z} \langle n|B|m\rangle \langle m|A|n\rangle \frac{1}{\omega - \omega_{mn} + i\delta}$$

Population of the states Matrix elements Line shape

Optical response functions from Kubo formula

When the system is driven by a perturbation $\mathcal{H}_{int} = -\hat{A}\cdot f(t)$

the response can be calculated $\langle \delta B(t)\rangle = \int \chi_{BA}(t-t')\, f(t')\, dt'$

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- works for a general (even interacting) system
- close to equilibrium: reponse comes from an expectation value calculated in equilibrium

Spectral decomposition:

$T \to 0$

$$\chi_{BA}(\omega) = -\frac{1}{\hbar}\sum_n \frac{\overbrace{\langle 0|B|n\rangle\langle n|A|0\rangle}^{M_{BA}}}{\omega-\omega_{n0}+i\delta} - \frac{\overbrace{\langle 0|A|n\rangle\langle n|A|0\rangle}^{M^*_{BA}}}{\omega+\omega_{n0}+i\delta}$$

$$= -\frac{2}{\hbar}\sum_n \frac{\omega_{n0}\,\mathrm{Re}\{\langle 0|B|n\rangle\langle n|A|0\rangle\} + i(\omega+i\delta)\,\mathrm{Im}\{\langle 0|B|n\rangle\langle n|A|0\rangle\}}{(\omega+i\delta)^2-\omega_{n0}^2}$$

$$= \chi^{Re}_{BA}(\omega) + i\,\chi^{Im}_{BA}(\omega)$$

$$\chi_{AB}(\omega) = \chi^{Re}_{BA}(\omega) - i\,\chi^{Im}_{BA}(\omega)$$

Applications of the Kubo formula

Time reversal symmetry $\quad \hat{A} \xrightarrow{T} \varepsilon_A \hat{A} \qquad \varepsilon_A = \pm 1$

$$\chi_{BA}(\omega, \underline{M}) = \chi_{AB}(\omega, -\underline{M})\,\varepsilon_A \varepsilon_B$$

$$\chi_{AA}(\omega, \underline{M}) = \chi_{AA}(\omega, -\underline{M})$$

$$\chi_{BA}(\omega, \underline{M}) = \chi_{BA}^{Re}(\omega, M) + i\,\chi_{BA}^{Im}(\omega, M)$$

$$= \varepsilon_A \varepsilon_B \left(\chi_{AB}^{Re}(\omega, -M) + i\,\chi_{AB}^{Im}(\omega, -M) \right)$$

$$= \varepsilon_A \varepsilon_B \left(\chi_{BA}^{Re}(\omega, -M) - i\,\chi_{BA}^{Im}(\omega, -M) \right)$$

$$\underline{\underline{\chi}}^{e} = \begin{bmatrix} \chi_{xx}^{Re} & \chi_{xy}^{Re} & \cdots \\ \chi_{xy}^{Re} & \chi_{yy}^{Re} & \\ \vdots & & \end{bmatrix} + \begin{bmatrix} 0 & \chi_{xy}^{Im} & \cdots \\ -\chi_{xy}^{Im} & 0 & \\ \vdots & & \end{bmatrix}$$

$$\chi_{\mu_x m_x}^{em} \qquad \varepsilon_{\mu_x} = 1, \quad \varepsilon_{m_x} = -1$$

when $M = 0 \Rightarrow \chi^{em, Re} = 0, \quad \chi_{m_x \mu_x}^{em, Im} = -\chi_{\mu_x m_x}^{em, Im}$

Applications of the Kubo formula

Charge susceptibility and dielectric response

$$P_x(\omega) = \varepsilon_0 \chi^c_{xx} E_x(\omega)$$

$$\chi_{\mu_x\mu_x}(\omega) E_x(\omega) = P_x(\omega)\cdot V$$

$$\chi^c_{xx} = \frac{1}{\varepsilon_0 V} \chi_{\mu_x\mu_x}$$

$$\chi_{xx} = -\frac{2}{\hbar\varepsilon_0 V}\sum_n \omega_{n0} \left|\langle n|\mu_x|0\rangle\right|^2 \frac{1}{(\omega+i\delta)^2-\omega_{n0}^2}$$

For non-interacting particles the wave function is a (anti-symmetrized) product of single particle states

$$\chi_{xx} = -\frac{2e^2}{\hbar\varepsilon_0}\frac{N}{V}\sum_n \omega_{n0} \left|\langle n|x|0\rangle\right|^2 \frac{1}{(\omega+i\delta)^2-\omega_{n0}^2}$$

single particle energies and wave functions

Oscillator strength:

$$f_{n0} = \frac{2m\omega_{n0}}{\hbar}\left|\langle n|x|0\rangle\right|^2$$

Applications of the Kubo formula

f-sum rule (integral of the intensity)

$$\sum_n f_{n0} = \sum_n \frac{2m\omega_{n0}}{\hbar} \left| \langle n | x | 0 \rangle \right|^2$$

$$= \frac{m}{\hbar^2} \sum_n \langle 0 | x | n \rangle (\varepsilon_n - \varepsilon_0) \langle n | x | 0 \rangle + \langle 0 | x | n \rangle (\varepsilon_n - \varepsilon_0) \langle n | x | 0 \rangle$$

$$= \frac{m}{\hbar^2} \sum_n \langle 0 | x | n \rangle \langle n | [H, x] | 0 \rangle - \langle 0 | [H, x] | n \rangle \langle n | x | 0 \rangle$$

$$= \frac{m}{\hbar^2} \langle 0 | [x, [H, x]] | 0 \rangle$$

general result

$$= \frac{m}{\hbar^2} \langle 0 | \left[x, \left[\frac{p^2}{2m}, x \right] \right] | 0 \rangle = 1$$

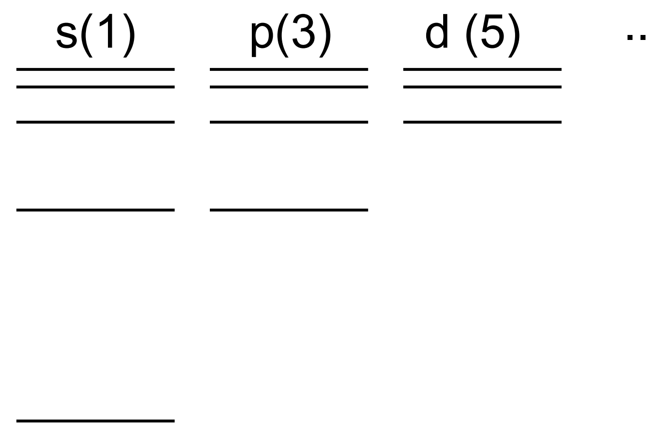
for electric dipole transitions

$$\sum_n f_{n0} = 1$$

$$\int_0^\infty \sigma'(\omega) d\omega = \int_0^\infty \varepsilon_0 \omega \chi''(\omega) d\omega = \frac{\pi n e^2}{2m} \sum_n f_{n0} = \frac{\pi n e^2}{2m}$$

Excitations of hydrogen (like) atoms

$$H_0 = \frac{p^2}{2m} - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}$$



Solution without the radiation

$$E_n = -\frac{Ze^2}{8\pi\varepsilon_0 a_0}\frac{1}{n^2}$$

$$\left|n,l,m\right\rangle = R(Zr/na_0)Y_l^m(\vartheta,\varphi)$$

Which transitions can be excited? (selection rules)

$$\left\langle n',l',m'\right|x\left|n,l,m\right\rangle = ?$$

$$= \int R(Zr/n'a_0)Y_{l'}^{m'}(\vartheta,\varphi)\,x\,R(Zr/na_0)Y_l^m(\vartheta,\varphi)\,dr\frac{d\Omega}{4\pi}$$

$$Y_1^{-1}(\theta,\varphi) = \frac{1}{2}\sqrt{\frac{3}{2\pi}}\cdot e^{-i\varphi}\cdot\sin\theta = \frac{1}{2}\sqrt{\frac{3}{2\pi}}\cdot\frac{(x-iy)}{r}$$

$$Y_1^{0}(\theta,\varphi) = \frac{1}{2}\sqrt{\frac{3}{\pi}}\cdot\cos\theta = \frac{1}{2}\sqrt{\frac{3}{\pi}}\cdot\frac{z}{r}$$

$$Y_1^{1}(\theta,\varphi) = -\frac{1}{2}\sqrt{\frac{3}{2\pi}}\cdot e^{i\varphi}\cdot\sin\theta = -\frac{1}{2}\sqrt{\frac{3}{2\pi}}\cdot\frac{(x+iy)}{r}$$

[wikipedia]

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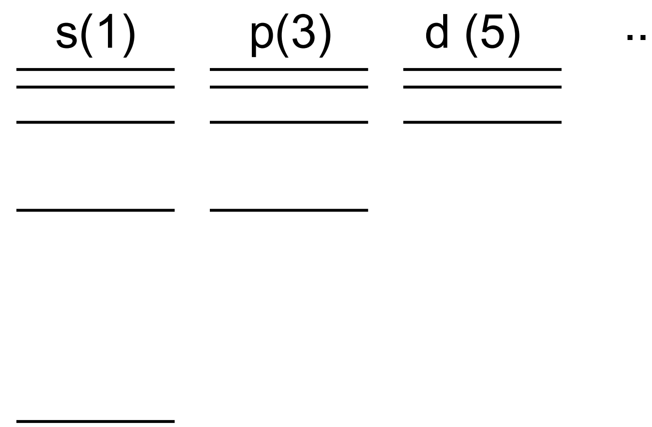

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$$\left\langle n', l', m'\right| x \left|n, l, m\right\rangle = ?$$

$$= \int R(Zr / n' a_0)Y_{l'}^{m'}(\vartheta, \varphi) x R(Zr / na_0)Y_l^m(\vartheta, \varphi) dr \frac{d\Omega}{4\pi}$$

$$\propto \int Y_{l'}^{m'} Y_1^{0,\pm 1} Y_l^m d\Omega$$

m'=m+0,±1

|l'-l|=±1

Excitations of hydrogen (like) atoms

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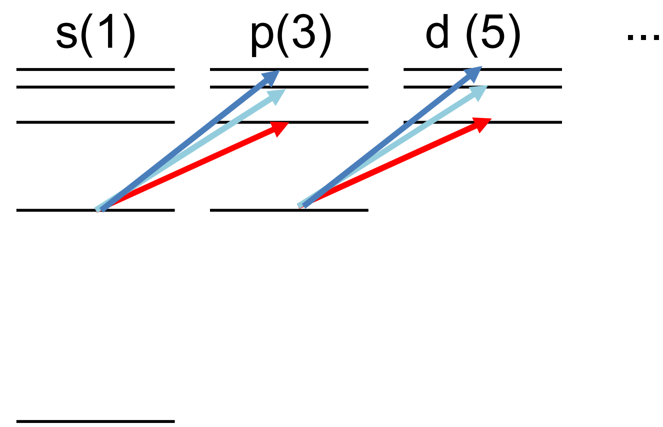

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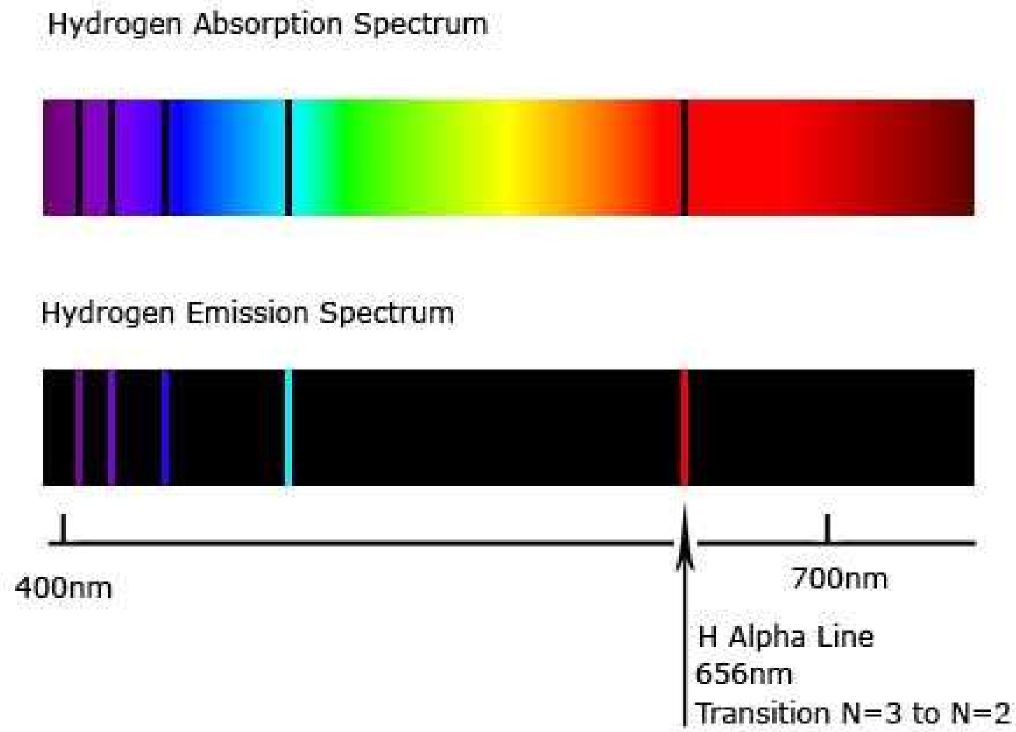


Balmer series (n=2):

$$\Delta E = R\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

Doppler broading of atomic lines

Doppler shif of the frequency of the absorption peak

$$f = f_0 \left(1 + \frac{v}{c}\right)$$

Maxwell-Boltzmann velocity distribution

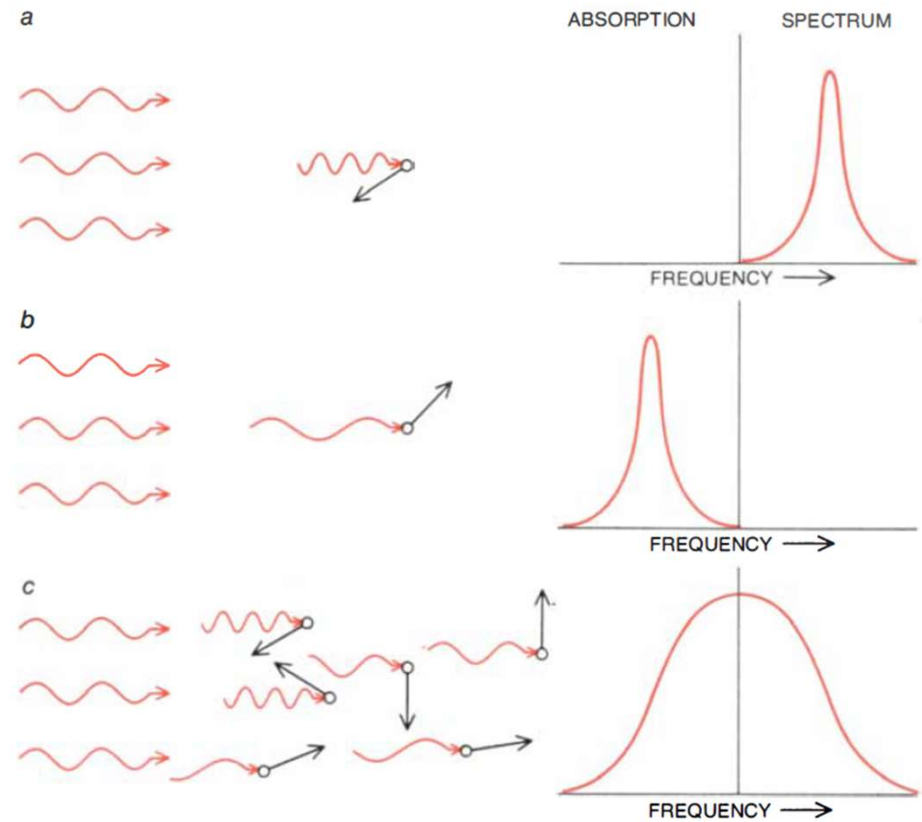
$$P_v(v)\,dv = \sqrt{\frac{m}{2\pi kT}}\,\exp\left(-\frac{mv^2}{2kT}\right)dv$$

Gaussian broadening of the absorption peak

$$P_f(f)\,df = P_v(v_f)\frac{dv}{df}\,df$$

$$P_f(f)\,df = \sqrt{\frac{mc^2}{2\pi kT f_0^2}}\,\exp\left(-\frac{mc^2(f-f_0)^2}{2kTf_0^2}\right)df;$$

$$\sigma_f = \sqrt{\frac{kT}{mc^2}}\,f_0$$

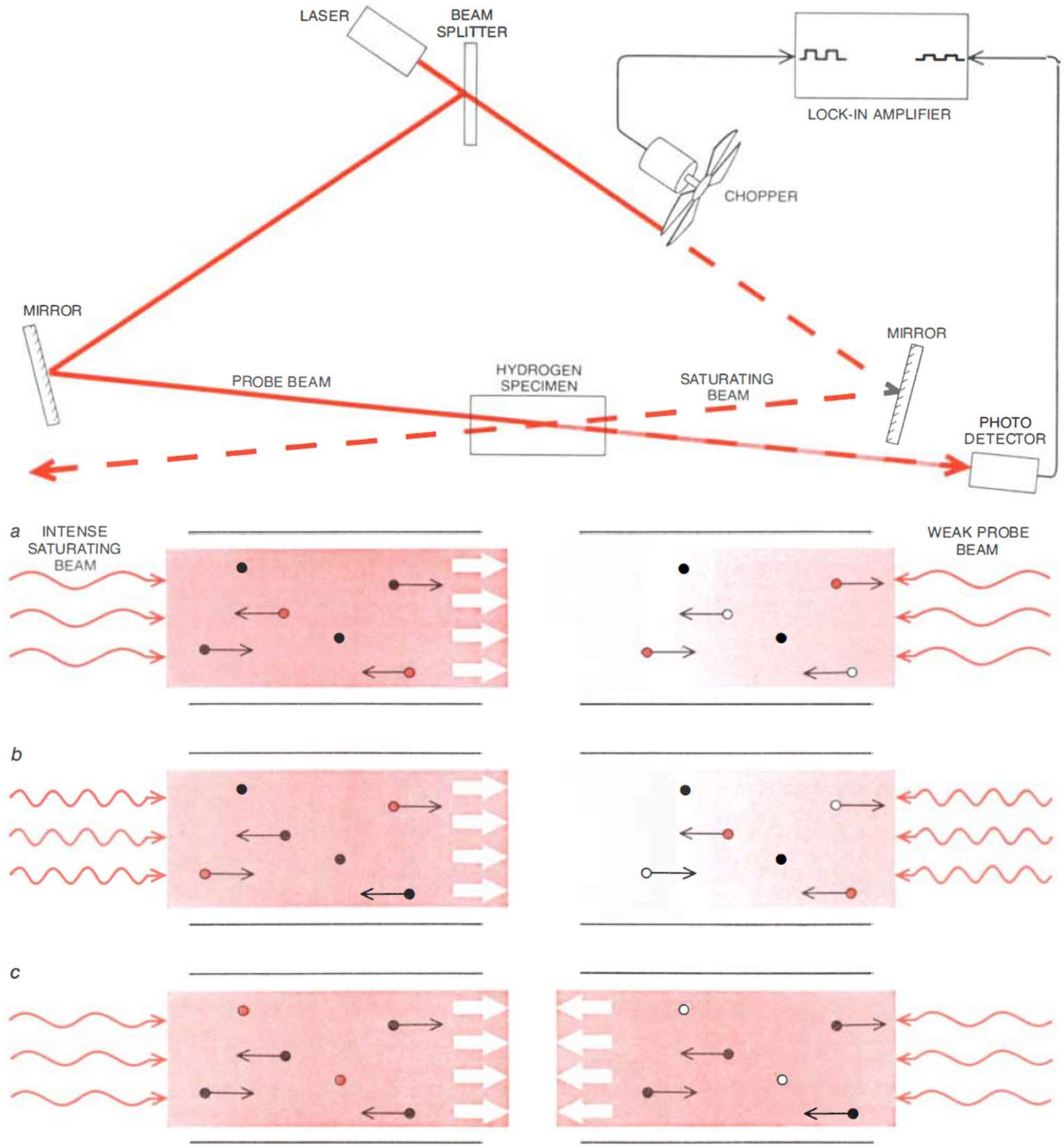


[Hansch Sci. Am. (1979)]

Broadening eg. for Ba_α (Balmer) at room temperature

$$\sqrt{\frac{25meV}{930MeV}}457THz \approx 5\cdot 10^{-6}\cdot 457THz \approx 2.2GHz$$

Saturation spectroscopy



[Hansch Sci. Am. (1979)]

Fine structure of the hydrogen atom

Relativistic corrections from Dirac equation split and shift the atomic levels, but J remains a good quantum number

Spectroscopic notation:

$$^{2S+1}L_J$$

The Ba$_\alpha$ line corresponds to excitations from n=2 to n=3
(notation in the figure nL_J)

$2S_{1/2}$
$2P_{1/2}$
$2P_{3/2}$

→

$3S_{1/2}$
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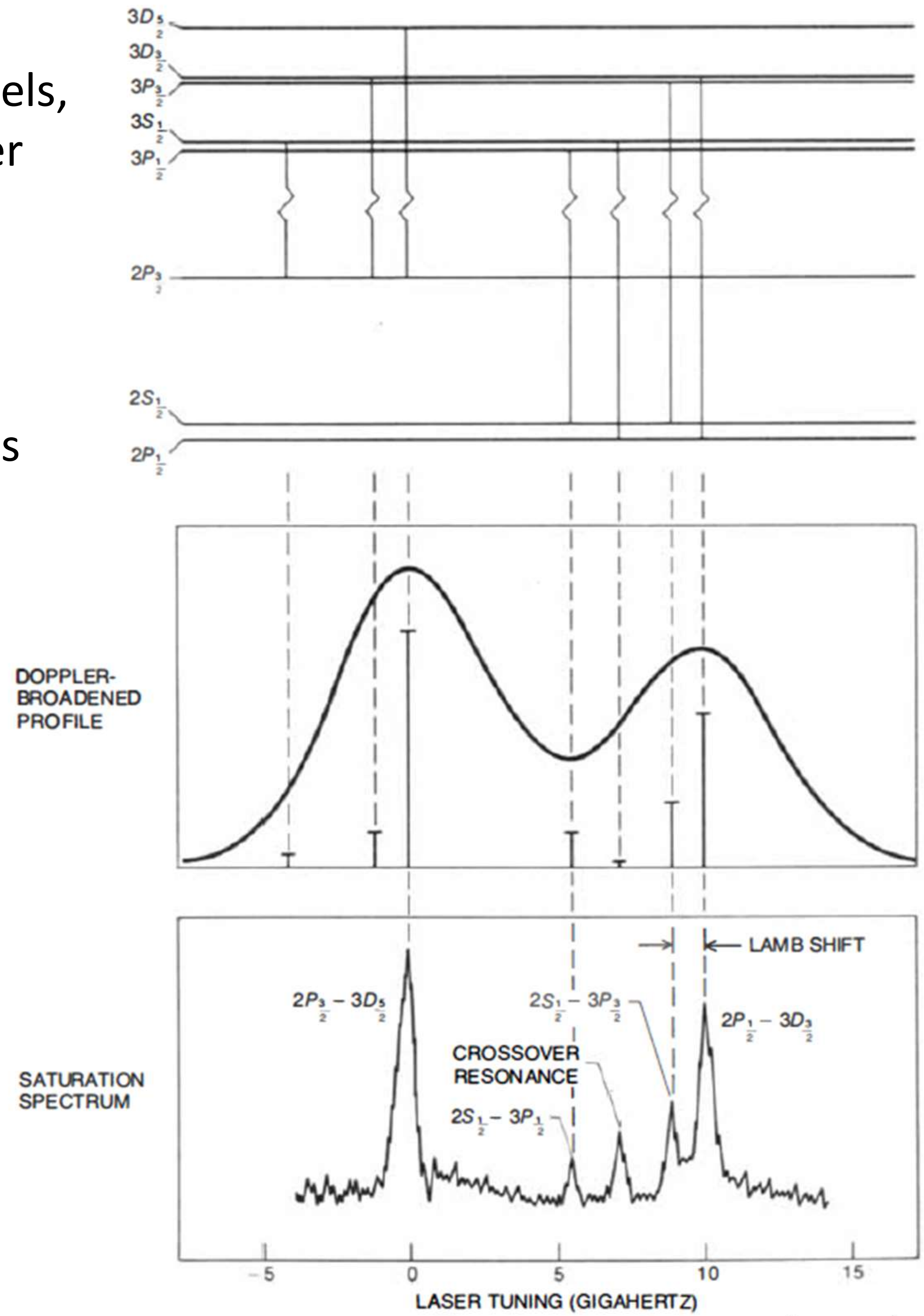


[Hansch Sci. Am. (1979)]

Dielectric response of solids

Charge susceptibility for ω>0:

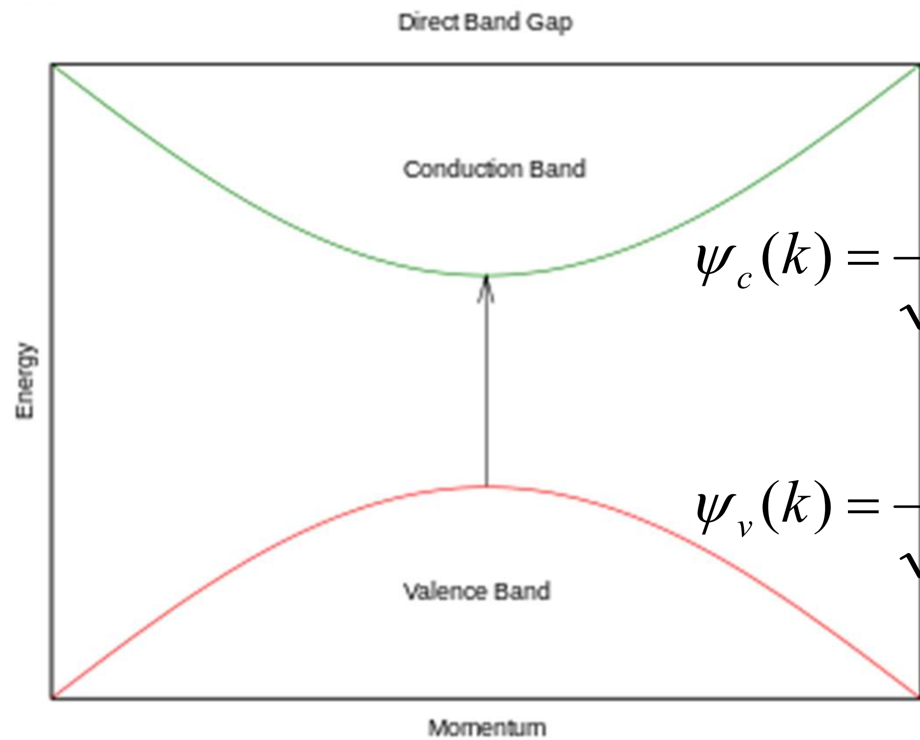
$$\chi_{xx} = \frac{e^2}{m\varepsilon_0}\frac{N}{V}\sum_n \frac{2m\omega_{n0}}{\hbar}\left|\langle n|x|0\rangle\right|^2\left(\frac{1}{\omega_{n0}^2-\omega^2}+i\frac{\pi}{2\omega}\delta(\omega_{n0}-\omega)\right)$$

Unperturbed Hamilton and its solution in terms of Bloch functions:

$$H_0 = \frac{p^2}{2m}+U(r)$$

$$U(r+R_n)=U(r)$$

$$\psi_n(k)=\frac{1}{\sqrt{V}}e^{ikr}u_{nk}(r)$$



$$\psi_c(k)=\frac{1}{\sqrt{V}}e^{ikr}u_{vc}(r)$$

$$\psi_v(k)=\frac{1}{\sqrt{V}}e^{ikr}u_{vk}(r)$$

[wikipedia]

Matrixelements:

$$\frac{p}{m}=\dot{x}=\frac{i}{\hbar}[H,x]$$

$$\langle n|x|0\rangle = \frac{1}{i\omega_{n0}m}\langle n|p|0\rangle$$

$$\langle ck'|p|vk\rangle = \int\frac{d^3r}{V}e^{-ik'r}u_{ck'}^*(r)\frac{\hbar}{i}\nabla e^{ikr}u_{vk}(r) = \int\frac{d^3r}{V}e^{-i(k'-k)r}u_{ck'}^*(r)\left(\hbar k+\frac{\hbar}{i}\nabla\right)u_{vk}(r)$$

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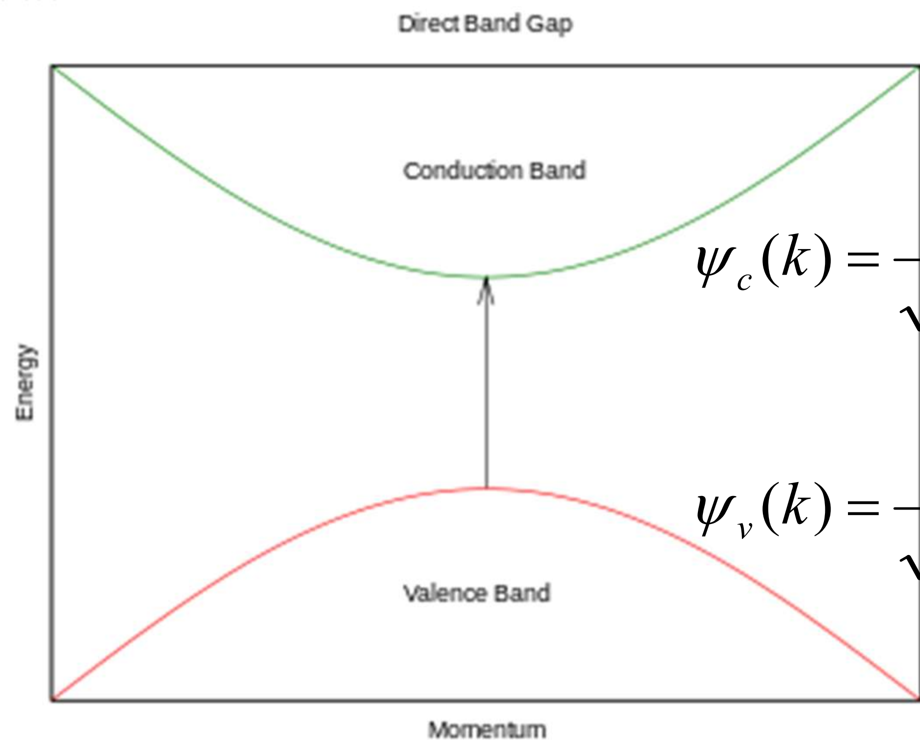

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[wikipedia]

Matrixelements:

$$\langle ck'|p|vk\rangle = \int\frac{d^3r}{V}e^{-i(k'-k)r}u^*_{ck'}(r)\left(\hbar k+\frac{\hbar}{i}\nabla\right)u_{vk}(r)$$

$$\sum_m F_m e^{iG_m r} = u^*_{ck'}(r)\left(\hbar k+\frac{\hbar}{i}\nabla\right)u_{vk}(r)$$

$$\langle ck'|p|vk\rangle = \sum_m\int\frac{d^3r}{V}F_m e^{-i(k'-k-G_m)r} \propto \sum_m \delta(k'-k-G_m)$$

Dielectric response of solids

Real part of the optical conductivity

$$\sigma' = \frac{N}{V}\frac{e^2}{m^2}\sum_k \frac{\pi}{\hbar\omega_{cv}}\left|\langle ck|p|vk\rangle\right|^2 \delta(\omega_{cv}-\omega)$$

$$\sigma' = \frac{N}{V}\frac{\pi e^2}{2m}\sum_k f\delta(\omega_{cv}-\omega)$$

$$f = \frac{2}{m\hbar\omega_{cv}}\left|\langle ck|p|vk\rangle\right|^2 = \frac{2m\omega_{cv}}{\hbar}\left|\langle ck|x|vk\rangle\right|^2$$

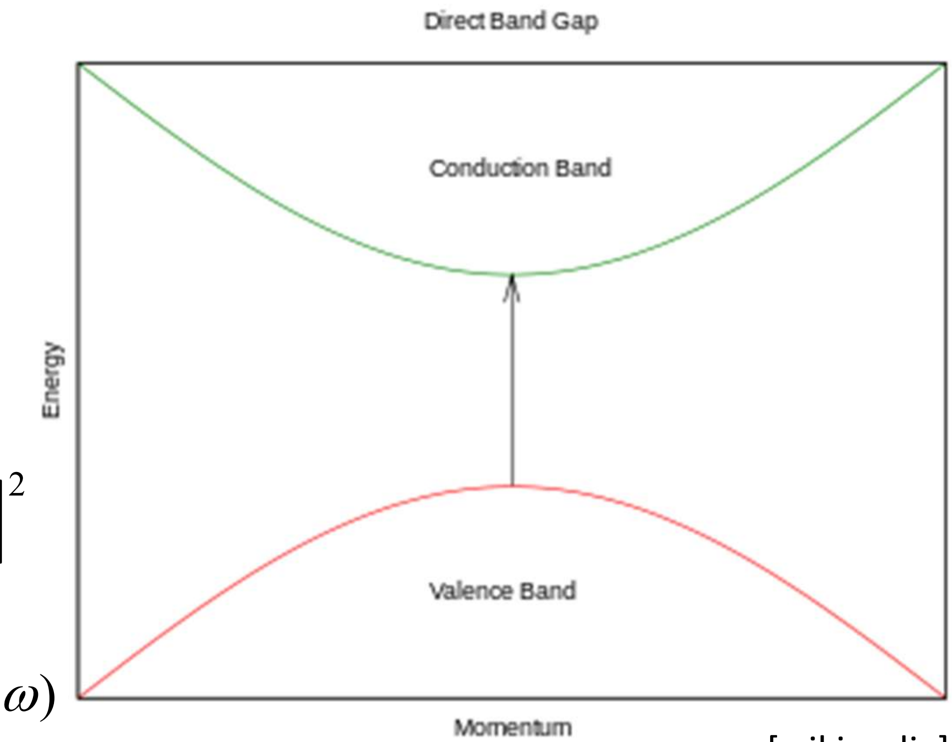
$$JDOS(\omega) = \sum_k \delta(\omega_{cv}(k)-\omega) = 2\int \frac{d^3k}{(2\pi)^3}\delta(\omega_{cv}(k)-\omega)$$

$$JDOS(\omega) = \int \frac{k^2 dk}{\pi^2}\delta(\omega_{cv}(k)-\omega)$$

$$\hbar\omega_{cv}(k) = \left(E_g + \frac{\hbar^2 k^2}{2m_c}\right) - \frac{\hbar^2 k^2}{2m_v} = E_g + \frac{\hbar^2 k^2}{2}\left(\frac{1}{m_c} + \frac{1}{|m_v|}\right)$$

$$JDOS(\omega) = \int \frac{d\omega_{cv}}{2\pi^2}\left(\frac{2m_r}{\hbar^2}\right)^{3/2}\sqrt{\omega_{cv} - E_g/\hbar}\,\delta(\omega_{cv}(k)-\omega)$$

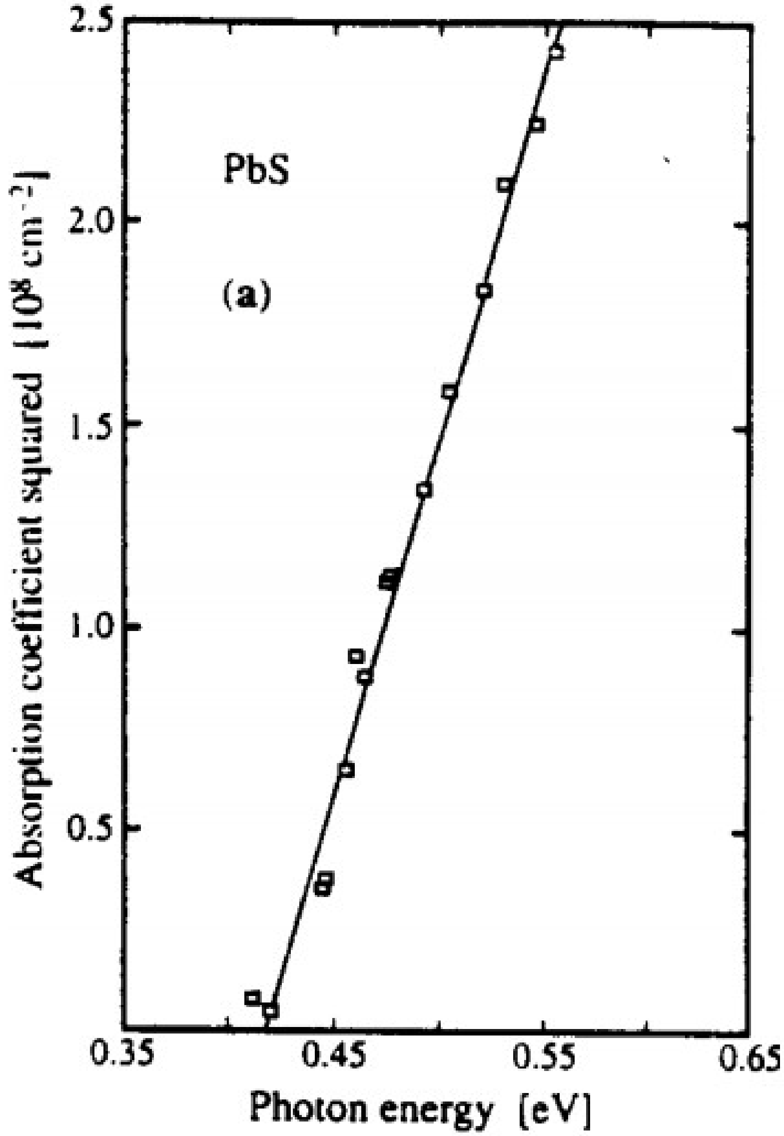
$$JDOS(\omega) = \frac{1}{2\pi^2}\left(\frac{2m_r}{\hbar^2}\right)^{3/2}\sqrt{\omega - E_g/\hbar}$$

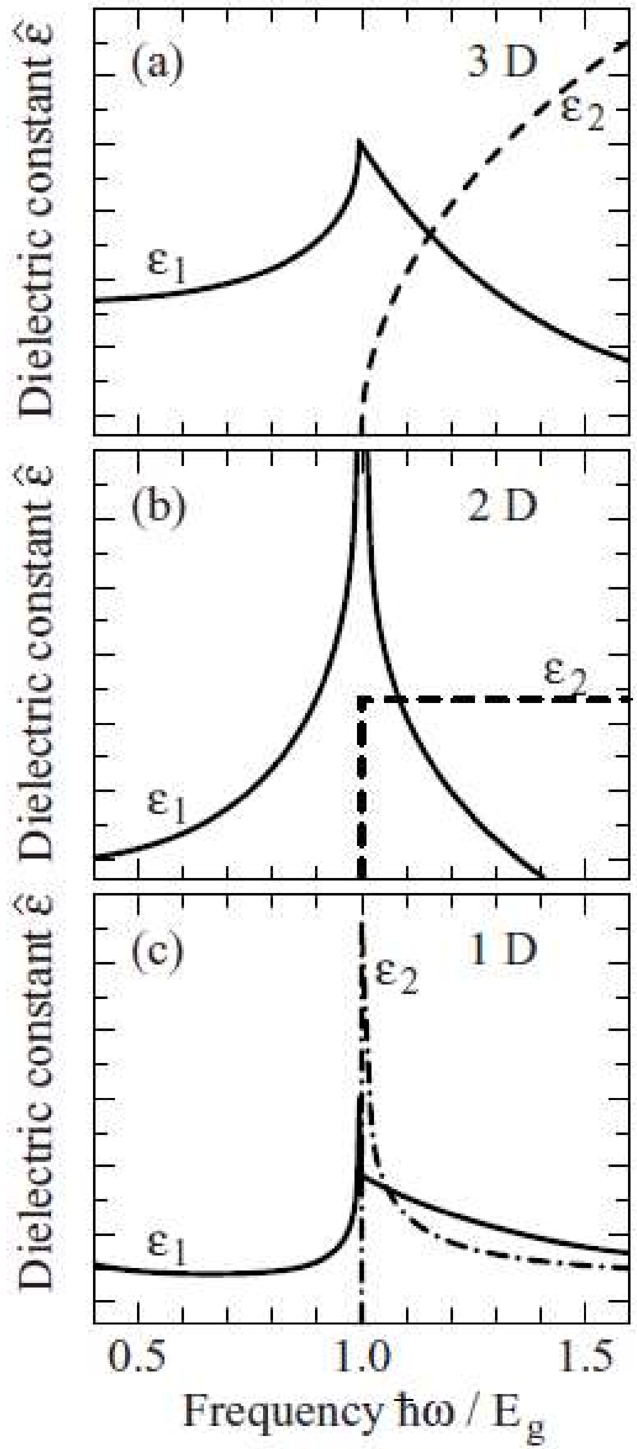


[wikipedia]

$$JDOS(\omega) = \frac{1}{2\pi^2}\left(\frac{2m_r}{\hbar^2}\right)^{3/2}\sqrt{\omega - E_g/\hbar}$$

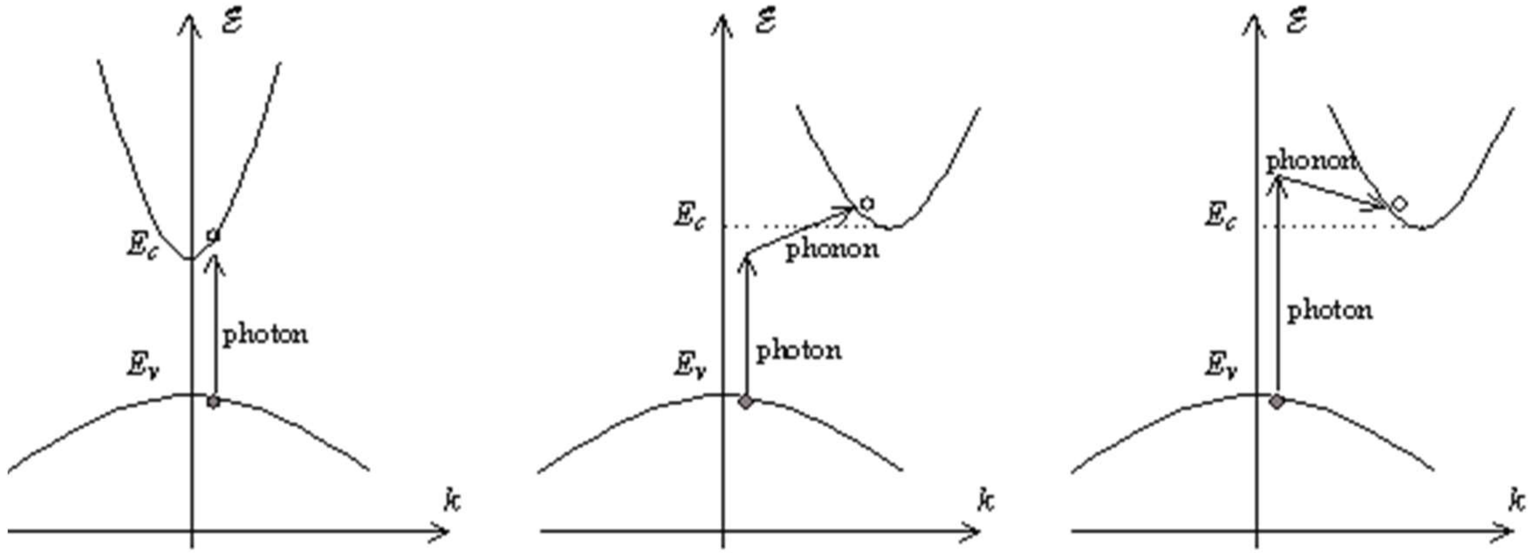
Direct band gap semiconductors

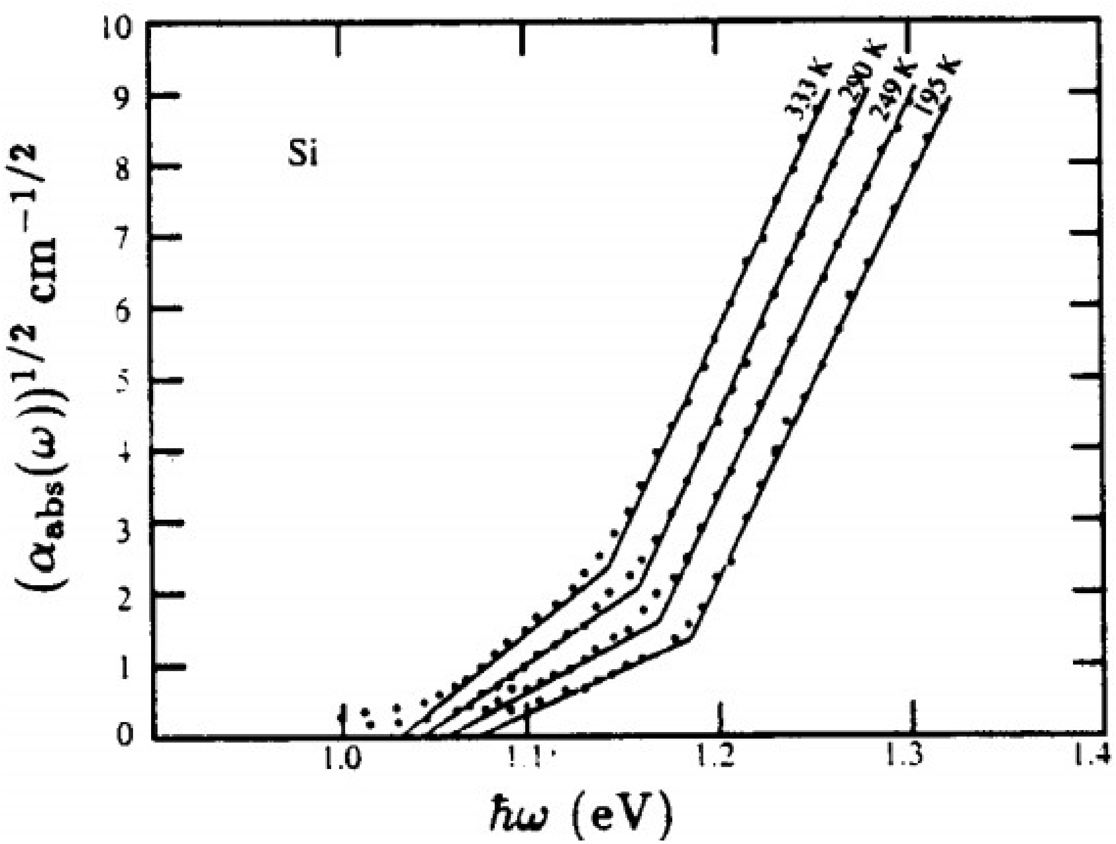




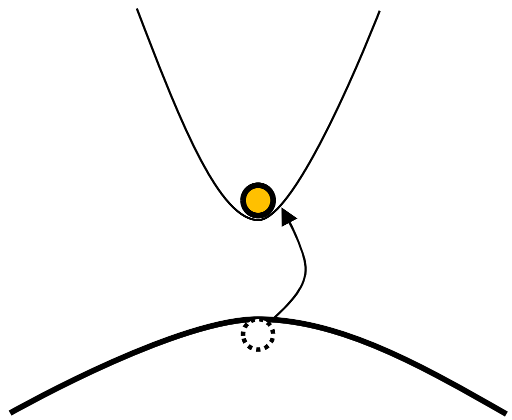
[Grüner&Dressel]

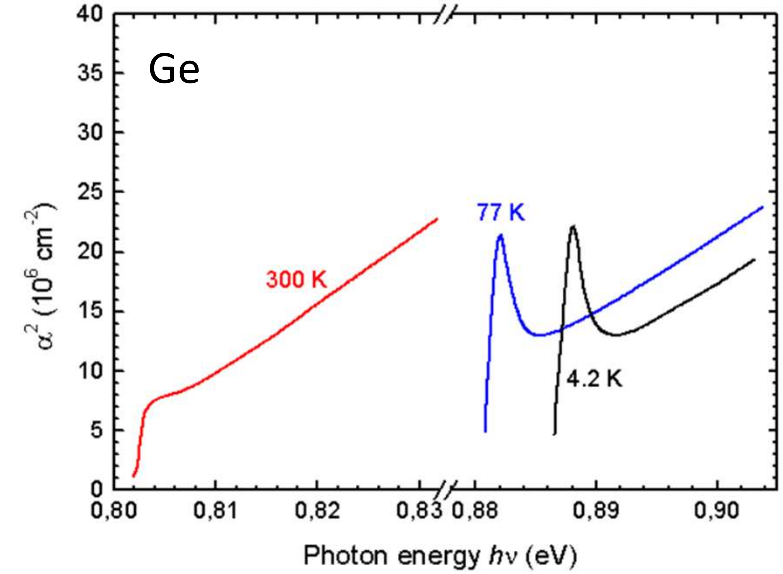
Indirect band gap semiconductors

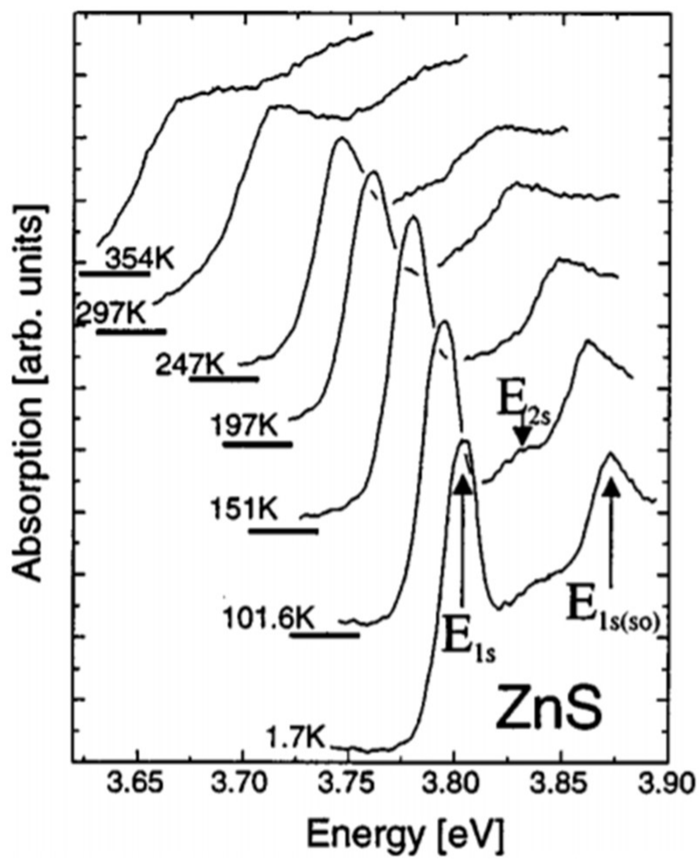


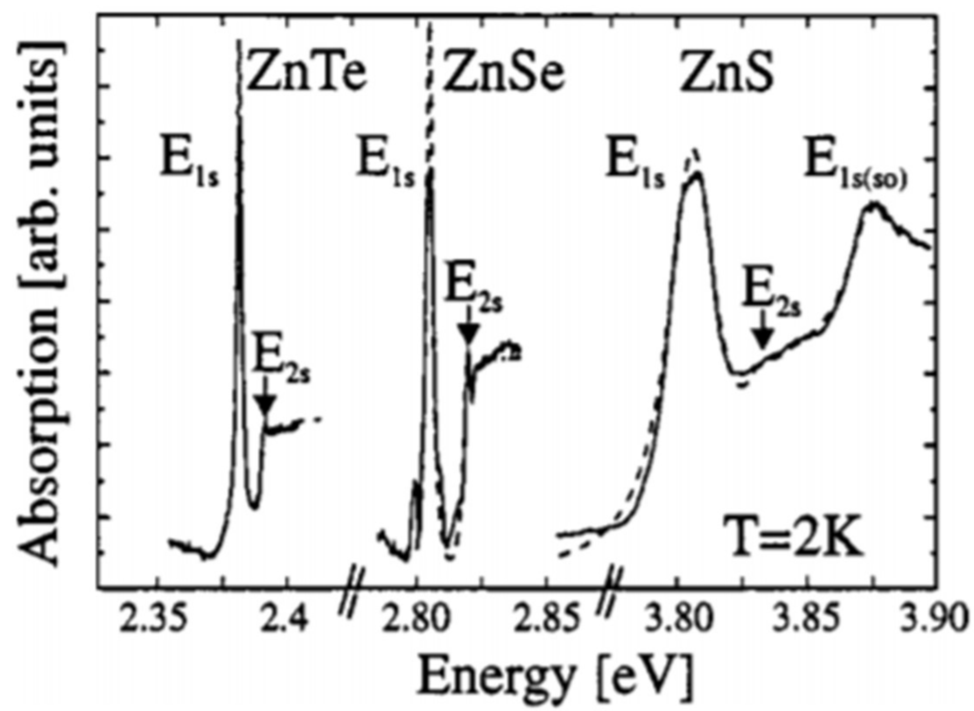


Excitons









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Applications of the Kubo formula

Sum rule (more generally)

$$\int_0^\infty \omega \chi_{AA}''(\omega) d\omega = -\frac{1}{\hbar} \sum_{n,m} \frac{e^{-\beta E_n} - e^{-\beta E_m}}{Z} \omega_{nm} \left| \langle n | A | m \rangle \right|^2$$

$$\int_0^\infty \omega \chi_{AA}''(\omega) d\omega = \frac{\pi}{2\hbar^2} \langle [A, [H, A]] \rangle_0$$