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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)

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

$$\boxed{\begin{aligned} H_0 &= \frac{p^2}{2m} + V \\ H_{\text{int}} &\approx \frac{e(pA + Ap)}{2m} + e\phi \end{aligned}}$$

Electromagnetic potentials:

$$\boxed{\begin{aligned} E &= -\nabla\phi - \frac{\partial A}{\partial t} \\ B &= \nabla \times A \end{aligned}}$$

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:

$$\left.\begin{aligned} \nabla \cdot \mathrm{E} &= \frac{1}{\varepsilon_0}\rho \\ \nabla \times \mathrm{B} &= \mu_0\left(\mathrm{j} + \varepsilon_0 \partial_t \mathrm{E}\right) \end{aligned}\right\} \begin{aligned} -\nabla^2\phi - \partial_t(\nabla \cdot \mathrm{A}) &= \frac{1}{\varepsilon_0}\rho \\ \nabla(\nabla \cdot \mathrm{A}) - \nabla^2 \mathrm{A} &= \mu_0 \mathrm{j} \end{aligned}$$

Dynamic potentials in the long wavelength limit

In the long wavelength limit, λ>>a:

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

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

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

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

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

Proof:

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

$$= -\partial_\nu \phi(0) + (\partial_\nu x_\alpha) E_\alpha(0) + \frac{1}{2} \partial_\nu (x_\alpha x_\beta)(\partial_\beta E_\alpha)\big|_0 - \partial_t \frac{1}{2} \varepsilon_{\nu\beta\gamma} B_\beta(0) x_\gamma$$

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

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

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

Proof:

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

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

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

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

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

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

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

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

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

Proof:

$$\partial_\alpha A_\alpha = \frac{1}{2} \varepsilon_{\alpha\beta\gamma} B_\beta(0)\, \partial_\alpha x_\gamma = \frac{1}{2} \underbrace{\varepsilon_{\alpha\beta\gamma}}_{\text{anti-symmetric}} B_\beta(0) \cdot \underbrace{\delta_{\alpha\gamma}}_{\text{symmetric}} = 0$$

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

Ligth-matter interaction in the long wavelength limit

Using the expansion:
$$\phi(\underline{x}) = \phi(0) - x_\alpha E_\alpha(0) - \frac{1}{2} x_\alpha x_\beta (\partial_\beta E_\alpha)\big|_0 + \dots$$
$$A_\alpha(\underline{x}) = \frac{1}{2}\varepsilon_{\alpha\beta\gamma} B_\beta(0) x_\gamma + \frac{1}{3}\varepsilon_{\alpha\gamma\delta}\, x_\beta (\partial_\beta B_\gamma)\big|_0\, x_\delta + \dots$$

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

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

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

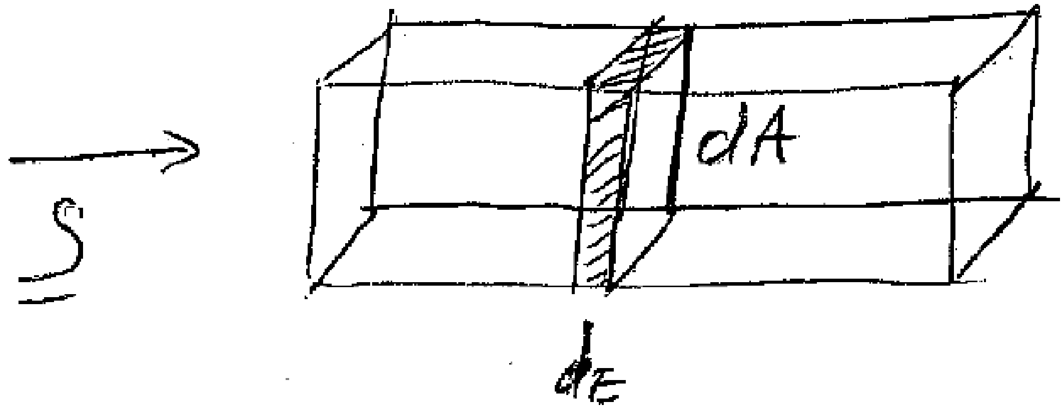
$$= e\phi(0) - e x_\alpha E_\alpha(0) - \frac{1}{3}\left[\frac{e}{2}\left(3x_\alpha x_\beta - (\underline{x})^2\delta_{\alpha\beta}\right)\right](\partial_\alpha E_\beta)\big|_0 - \frac{e\hbar}{2m}\left(L_\alpha/\hbar + g\, S_\alpha/\hbar\right) B_\alpha(0)$$

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

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

Absorption from time-dependent perturbation theory

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



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

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

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

Fermi's golden rule: $W_{n \to m} = \frac{2\pi}{\hbar} |\langle m | H_{int} | n \rangle|^2 \delta(E_m - E_n - \hbar\omega)$

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

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

$$\chi_{BA}(t) = \frac{i}{\hbar}\theta(t)\sum_n \langle n|\frac{e^{-\beta\mathcal{H}}}{Z}\Big(e^{\frac{i}{\hbar}\mathcal{H}t}B\underset{\sum_m |m\rangle\langle m|}{\uparrow}e^{-\frac{i}{\hbar}\mathcal{H}t}A - Ae^{\frac{i}{\hbar}\mathcal{H}t}\underset{\sum_m |m\rangle\langle m|}{\uparrow}Be^{-\frac{i}{\hbar}\mathcal{H}t}\Big)|n\rangle$$

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

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

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

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Spectral decomposition:

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

Population of the states   Matrix elements   Line shape

Optical response functions from Kubo formula

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

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

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

Spectral decomposition:

$T \to 0$

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

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

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

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

Applications of the Kubo formula

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

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

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

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

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

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

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

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

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)

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

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

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

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

general result

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

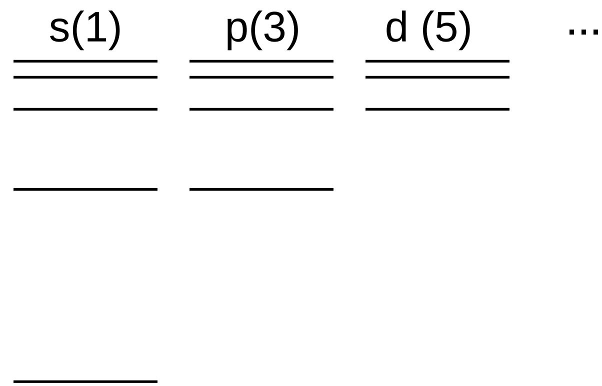
for electric dipole transitions

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

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

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]

Excitations of hydrogen (like) atoms

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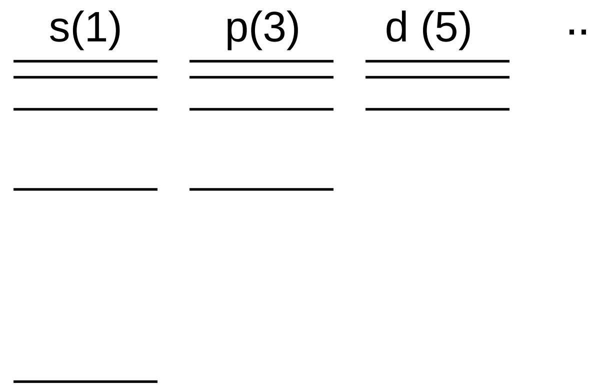

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$$= \int R(Zr/n'a_0)Y_{l'}^{m'}(\vartheta,\varphi)\, x\, R(Zr/na_0)Y_l^m(\vartheta,\varphi)\, dr\, \frac{d\Omega}{4\pi}$$

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

m’=m+0,±1

|l’-l|=±1

Excitations of hydrogen (like) atoms

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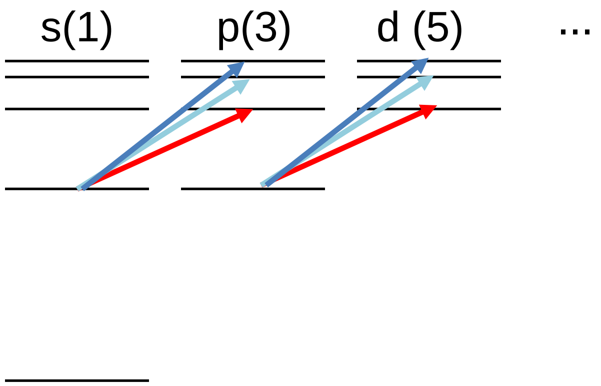


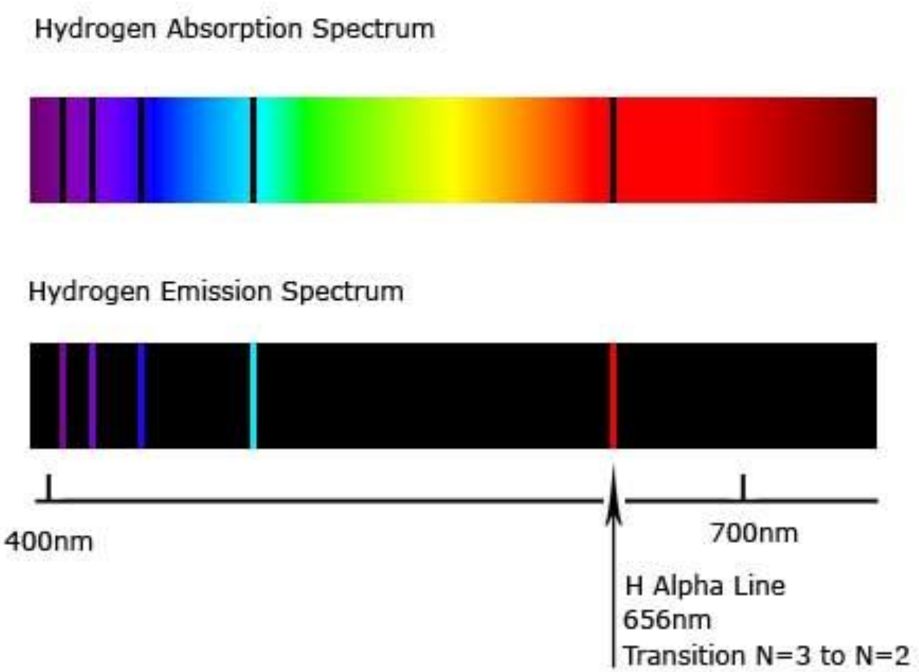
Solution without the radiation

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

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

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

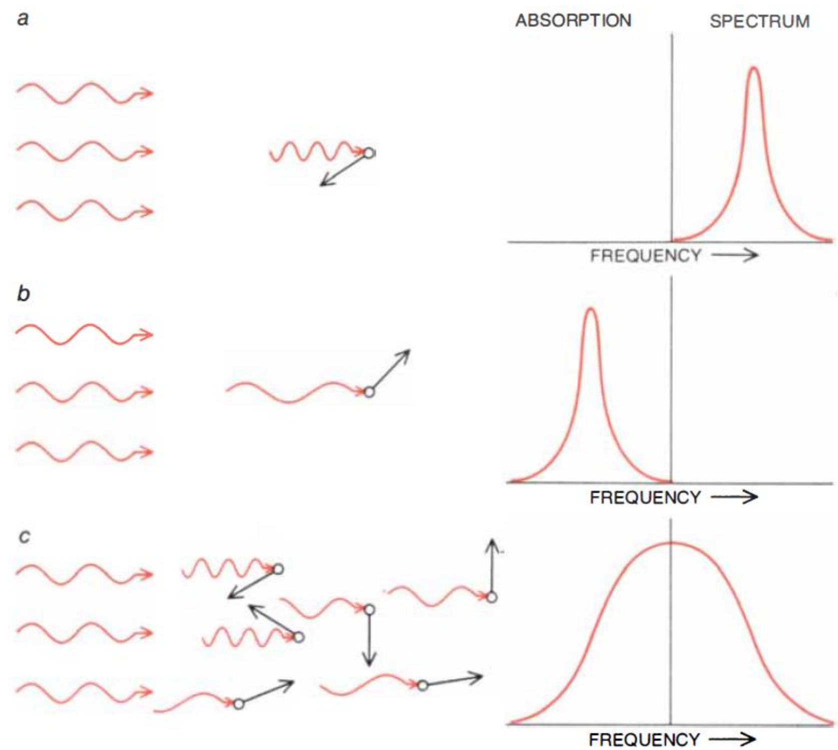
$$P_v(v)\,dv = \sqrt{\frac{m}{2\pi kT}}\,\exp\left(-\frac{mv^2}{2kT}\right)dv$$

Gaussian broadening of the absorption peak

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

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

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

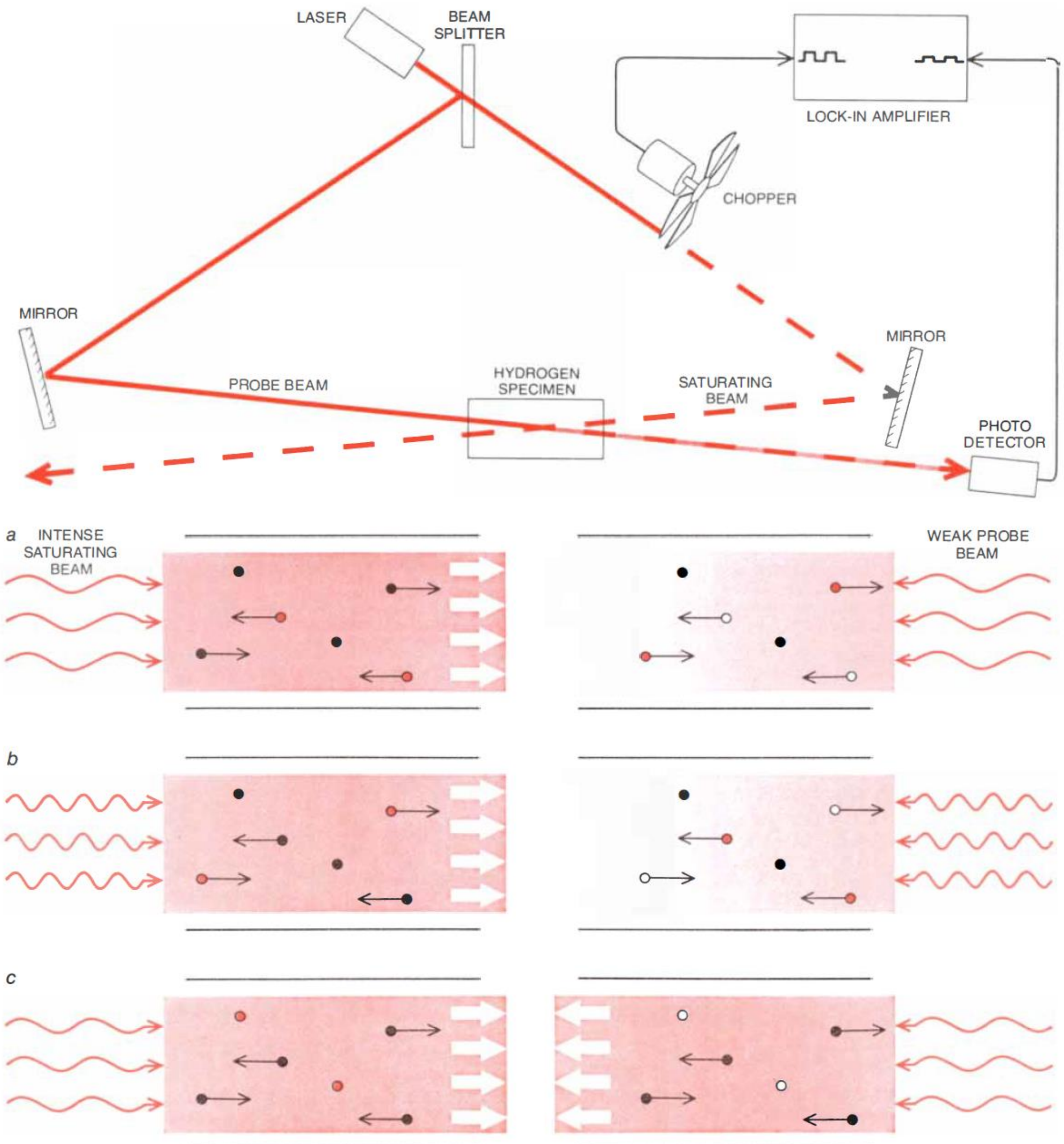


[Hansch Sci. Am. (1979)]

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

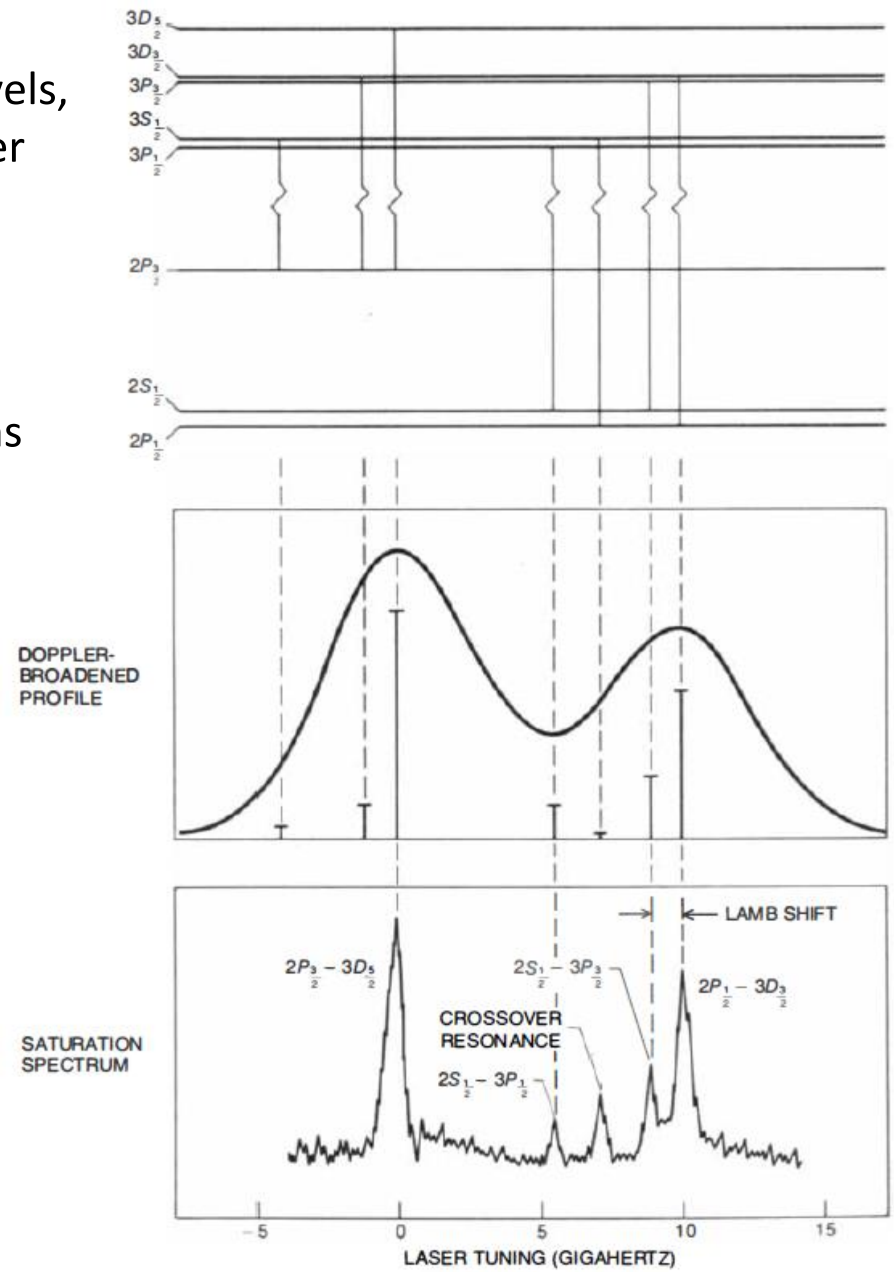
Relativistic corrections from Dirac equation split and shift the atomic levels, but J remains a good quantum number

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)

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



[Hansch Sci. Am. (1979)]

Dielectric response of solids

Charge susceptibility for ω>0:

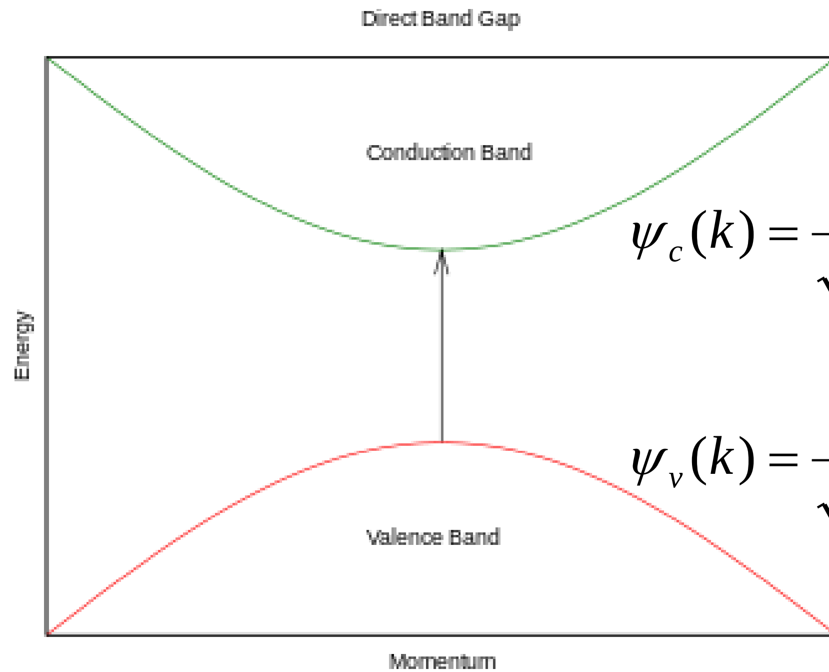
$$\chi_{xx} = \frac{e^2}{m\varepsilon_0}\frac{N}{V}\sum_n \frac{2m\omega_{n0}}{\hbar}\left|\langle n|x|0\rangle\right|^2\left(\frac{1}{\omega_{n0}^2-\omega^2}+i\frac{\pi}{2\omega}\delta(\omega_{n0}-\omega)\right)$$

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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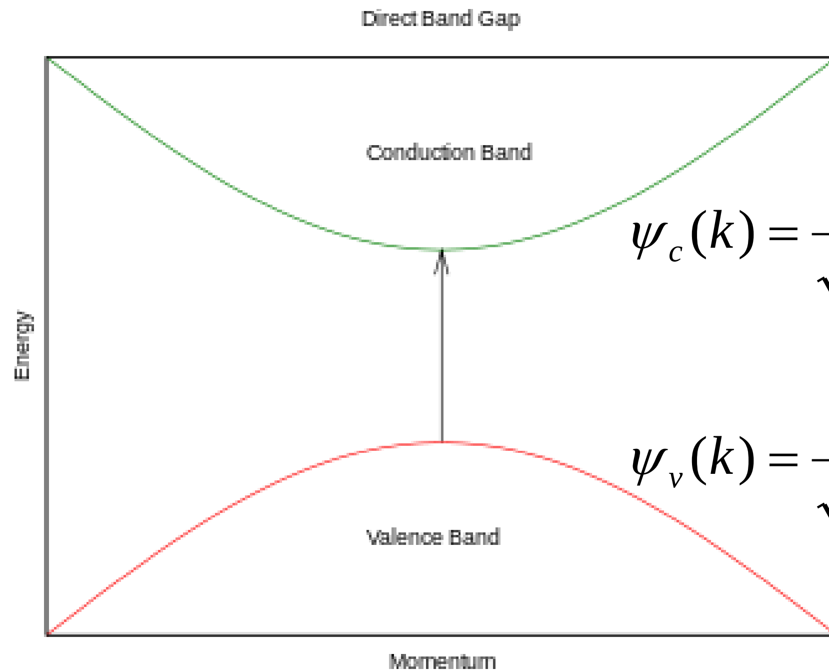

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[wikipedia]

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

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

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

Dielectric response of solids

Real part of the optical conductivity

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

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

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

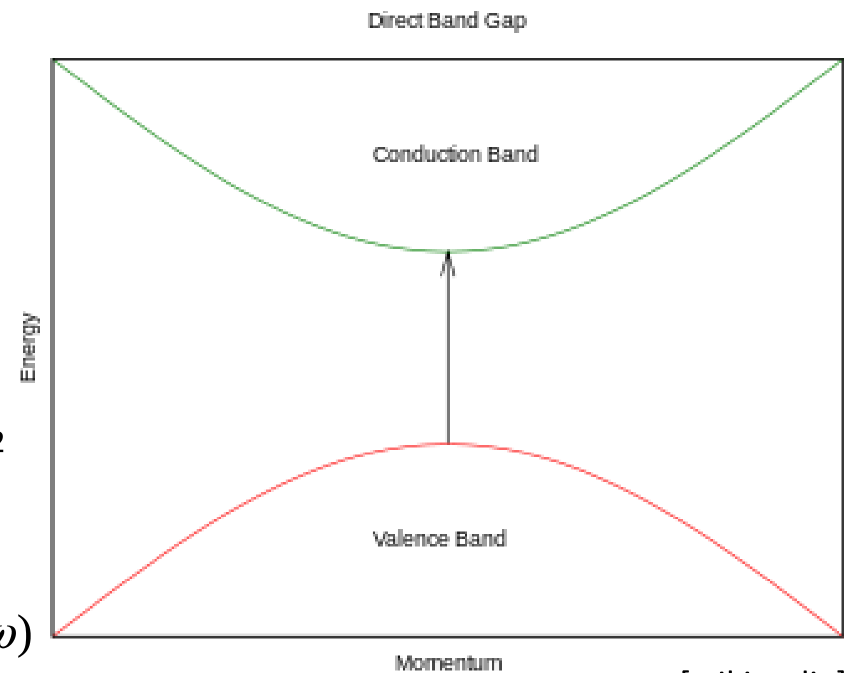
$$JDOS(\omega) = \sum_k \delta(\omega_{cv}(k)-\omega) = 2\int\frac{d^3k}{(2\pi)^3}\delta(\omega_{cv}(k)-\omega)$$

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

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

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

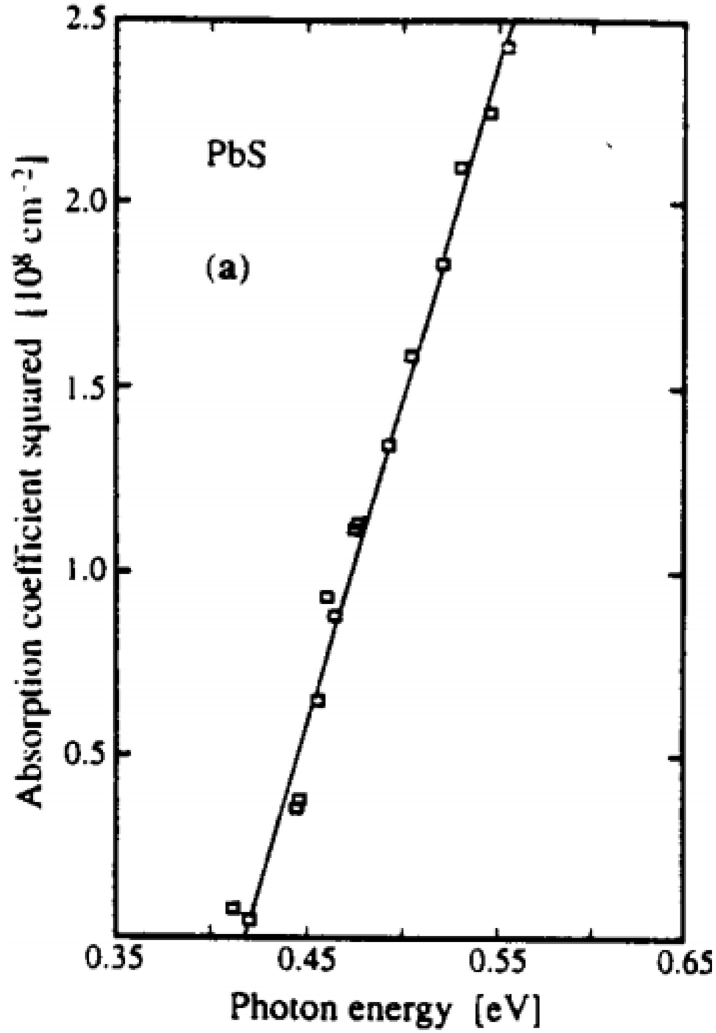
$$JDOS(\omega) = \frac{1}{2\pi^2}\left(\frac{2m_r}{\hbar^2}\right)^{3/2}\sqrt{\omega-E_g/\hbar}$$

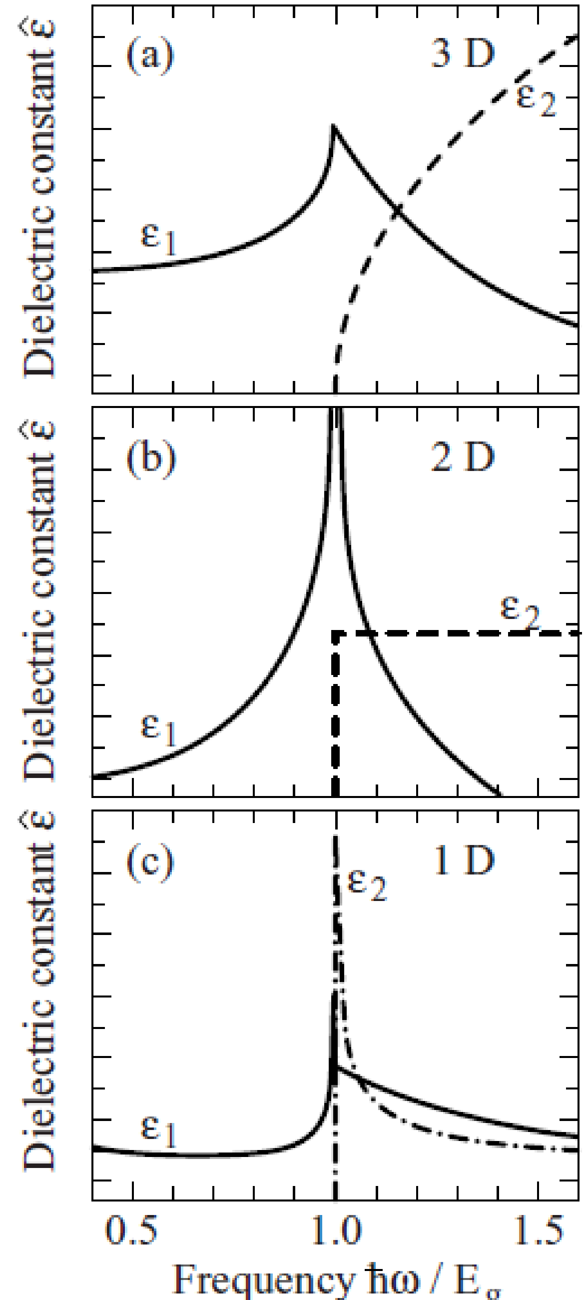


[wikipedia]

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

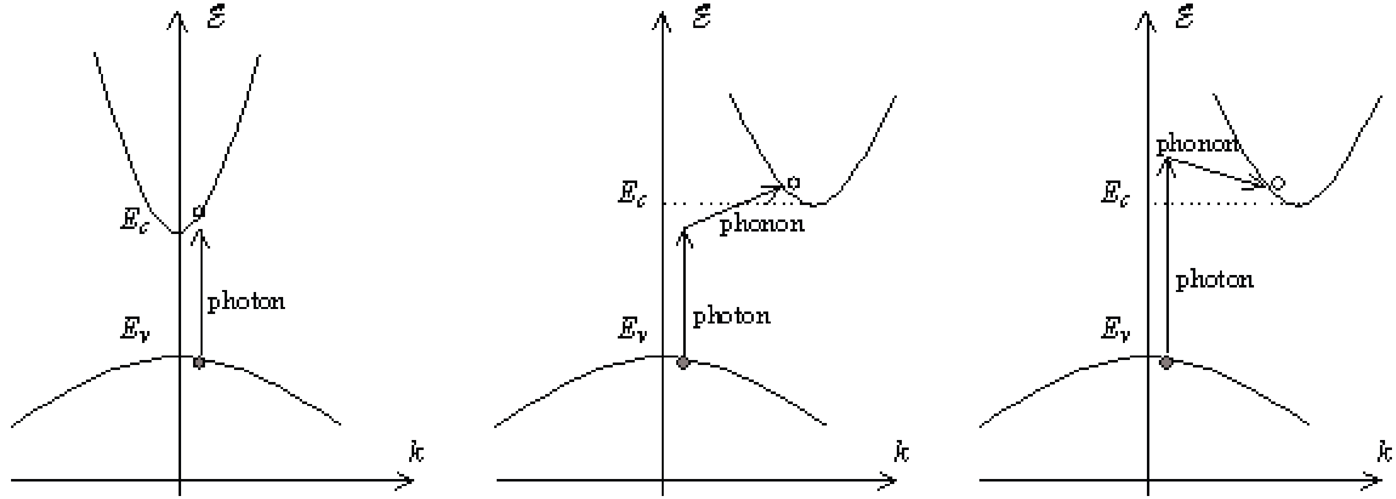
Direct band gap semiconductors

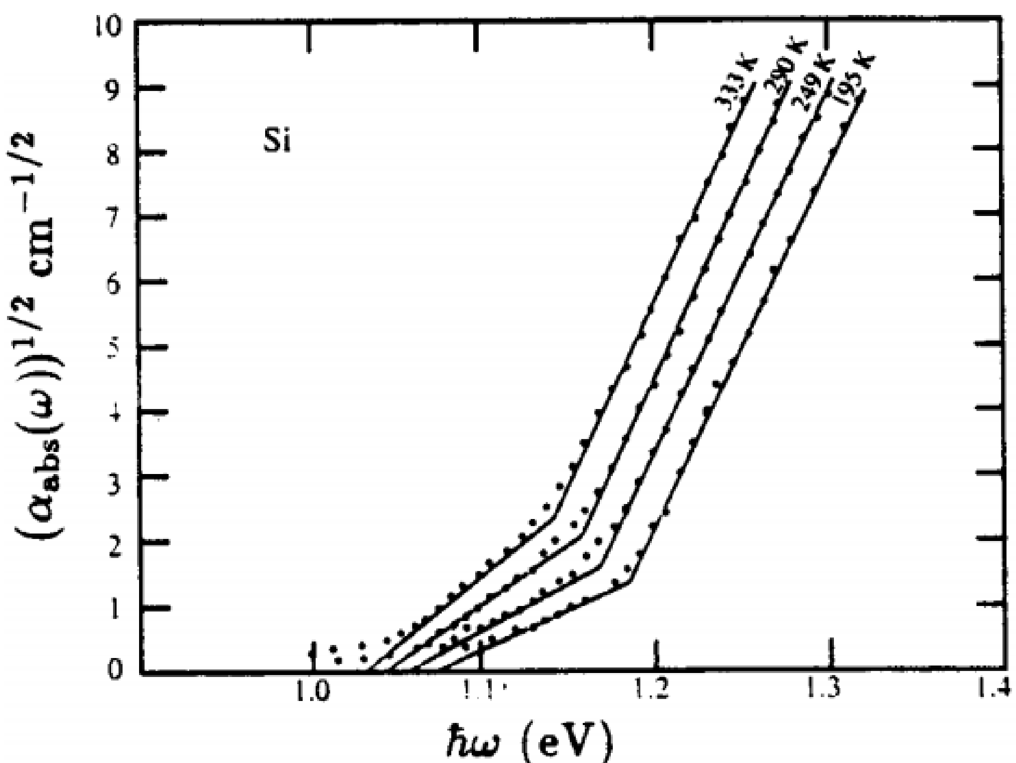




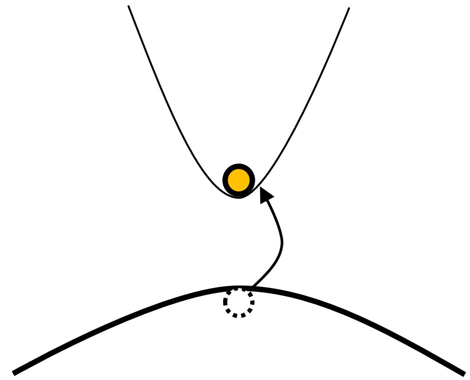
[Grüner&Dressel]

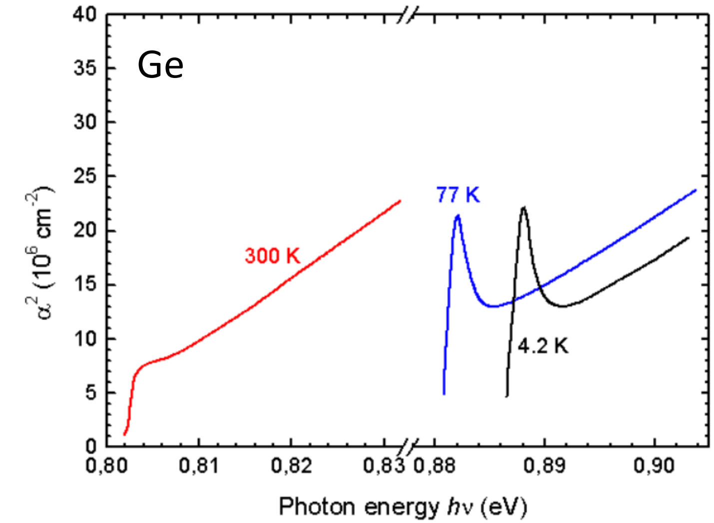
Indirect band gap semiconductors

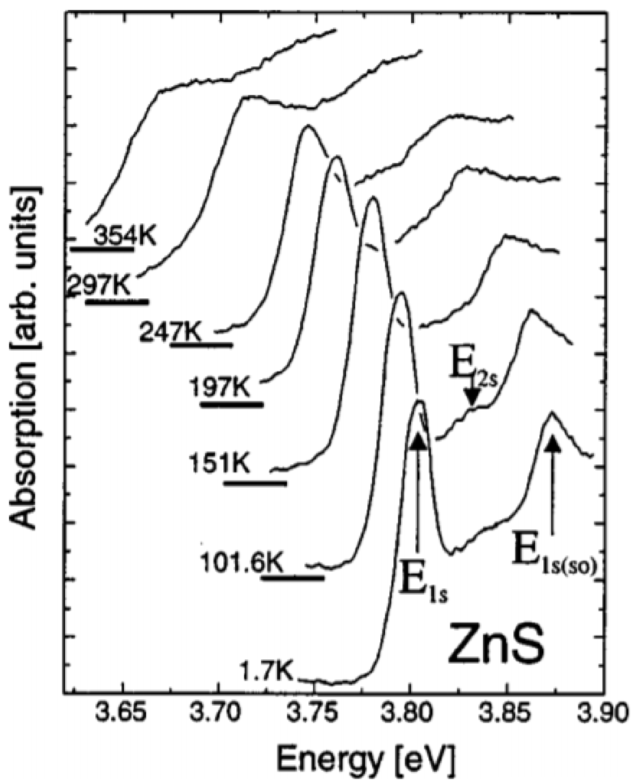


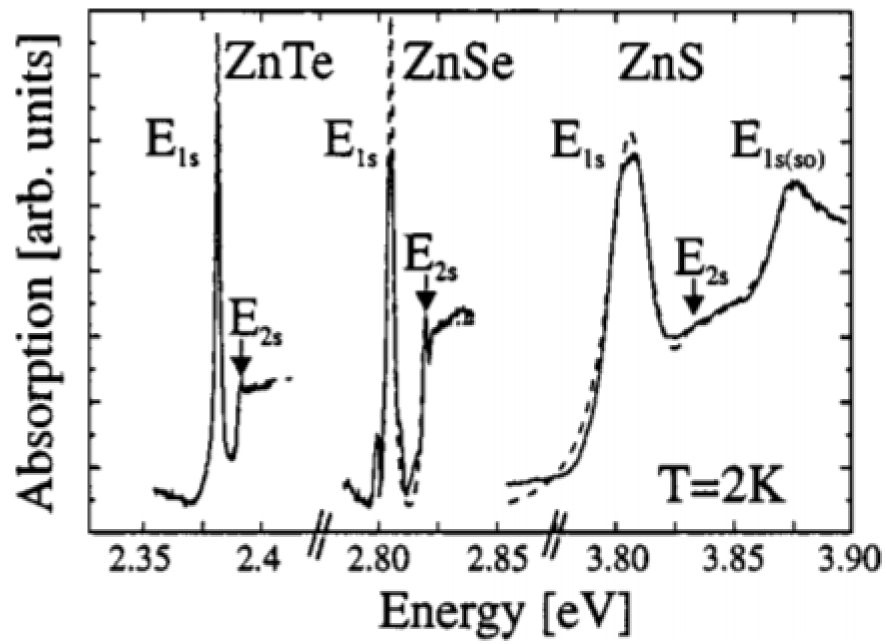


Excitons









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