Corrections relativistes à l'atome de H

(structure fine)

structure principal

$$E_n = -\frac{Ry}{n^2} \qquad n = 1, 2, \ldots$$

corrections de SF

$$\alpha = \frac{\hbar}{m_e a_0} \simeq \frac{1}{137}$$

$s = 1/2$

$s(s+1)$

coupLage spin - orbite

$$\rightarrow \quad \Delta E^{(SO)}_{nlsj} = -\frac{E_n}{2} \frac{\alpha^2 Z^4}{n\,l(l+1)(l+\frac{1}{2})} \left[j(j+1) - l(l+1) - \frac{3}{4} \right]$$

correction relativiste à l'énergie cinétique

$$\rightarrow \quad \Delta E^{(rel)}_{nl} = -E_n \frac{Z^4 \alpha^2}{n^2} \left[\frac{3}{4} - \frac{n}{l+1/2} \right]$$

terme de Darwin

$$\rightarrow \quad \Delta E^{(D)}_{nl} = -E_n \frac{Z^4 \alpha^2}{n} \delta_{l,0}$$

$$\Delta E^{(SF)}_{nj} = \Delta E^{(SO)} + \Delta E^{(rel)} + \Delta E^{(D)}$$

$$= \ldots = \underbrace{\frac{|E_n| \alpha^2 Z^4}{n^2}}_{>0} \underbrace{\left(\frac{3}{4} - \frac{n}{j+1/2} \right)}_{<0} \quad \underline{\underline{<0}}$$

$\dfrac{n}{j+1/2} > 1$

$n \geq l+1 \qquad l = 0, \ldots, n-1$

$j = \ell - \frac{1}{2}, \quad \ell + \frac{1}{2} \quad \leq \ell + \frac{1}{2}$

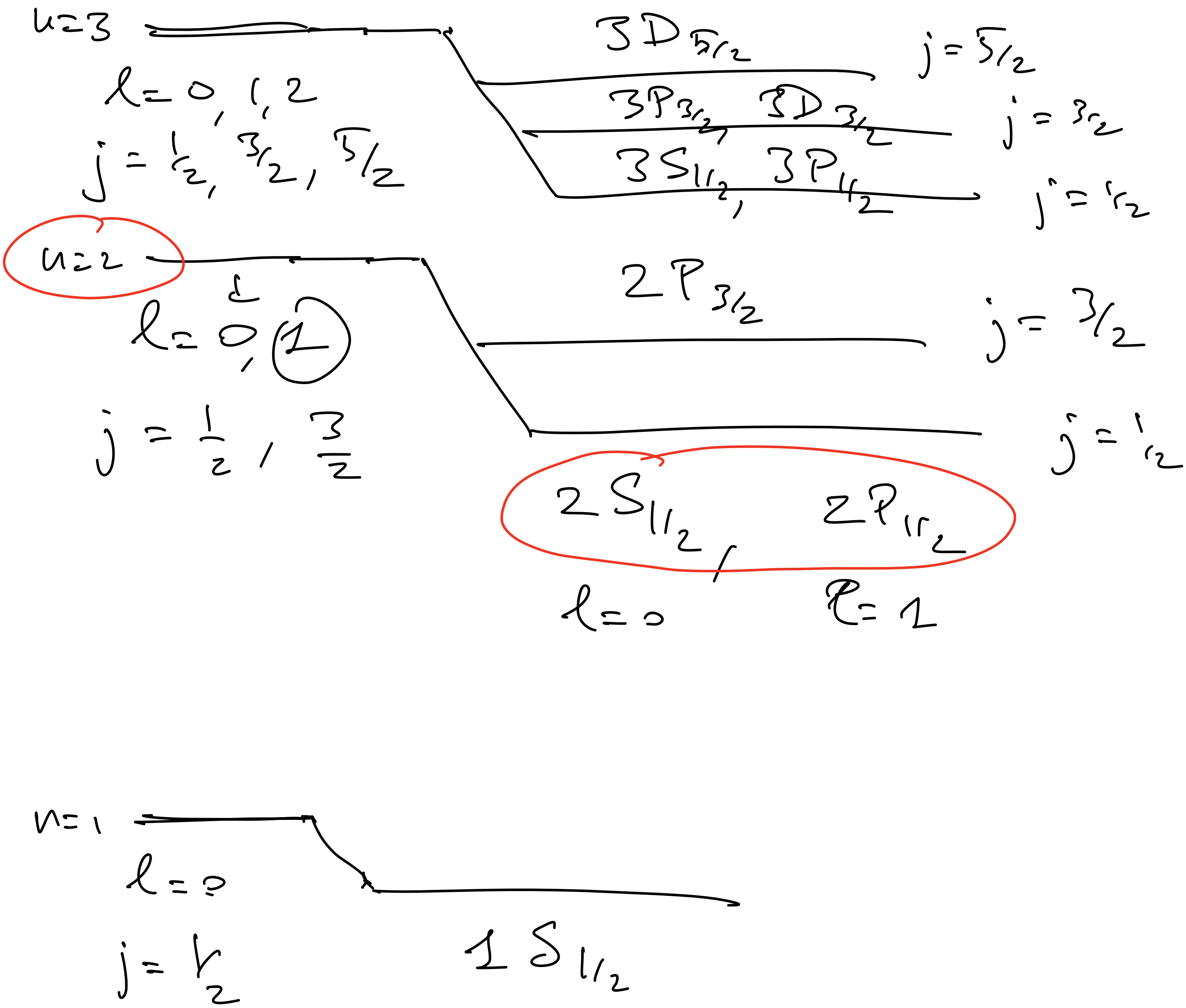
$n \geq \ell + 1 = \ell + \frac{1}{2} + \frac{1}{2} \geq \underline{\underline{j + \frac{1}{2}}}$

$|n \ell s ; \overset{1}{j} m_j\rangle \longrightarrow$ notation spectroscopique

$n L_j$

S, P, D, ...

$\ell = 0, 1, 2, \ldots$



n=3
l = 0, 1, 2
j = 1/2, 3/2, 5/2
3D5/2
j = 5/2
3P3/2, 3D3/2
j = 3/2
3S1/2, 3P1/2
j = 1/2
n=2
l = 0, 1
j = 1/2, 3/2
2P3/2
j = 3/2
j = 1/2
2S1/2, 2P1/2
l = 0
l = 1
n=1
l = 0
j = 1/2
1S1/2

Interaction lumière (champs e.m.) - atomes : bases de la spectroscopie

Rappels d'e.m. $\quad (\vec{E}, \vec{B}) \leftarrow (\vec{A}, \phi)$

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

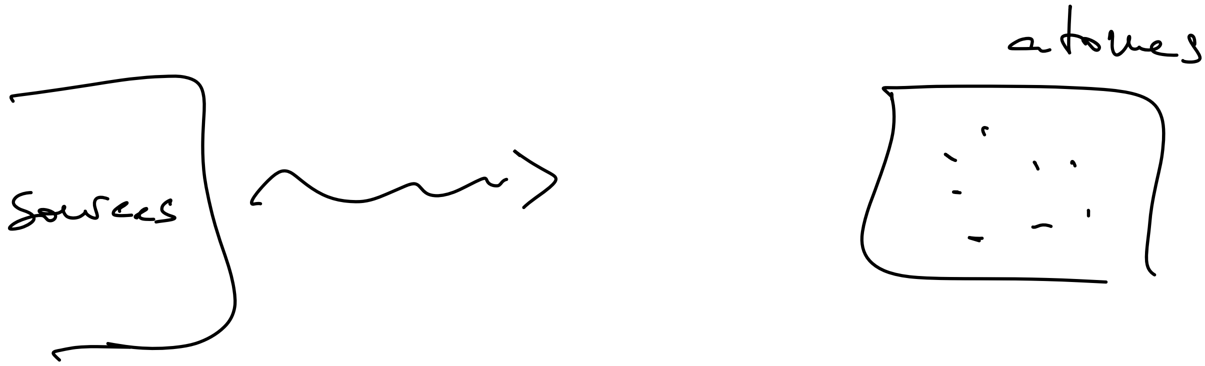
$$\vec{B}(\vec{r},t) = \vec{\nabla} \times \vec{A}(\vec{r},t)$$

jauge de Coulomb $\boxed{\vec{\nabla}\cdot\vec{A} = 0}$

$$\vec{\nabla}\cdot\vec{E} = \rho/\epsilon_0$$

$$\rightarrow \boxed{\vec{\nabla}^2 \phi = -\rho/\epsilon_0}$$

loin des charges / sources



$$\phi \simeq 0$$

$$\boxed{\nabla^2 \vec{A} - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\vec{A} = 0} \Longleftarrow$$

complexe conjugué

$$A(\vec{r},t) = \frac{A_0}{2}\left[\vec{\epsilon}\, e^{i(\vec{k}\cdot\vec{r}-\omega t)} + c.c.\right]$$

$$\omega = c|\vec{k}|$$

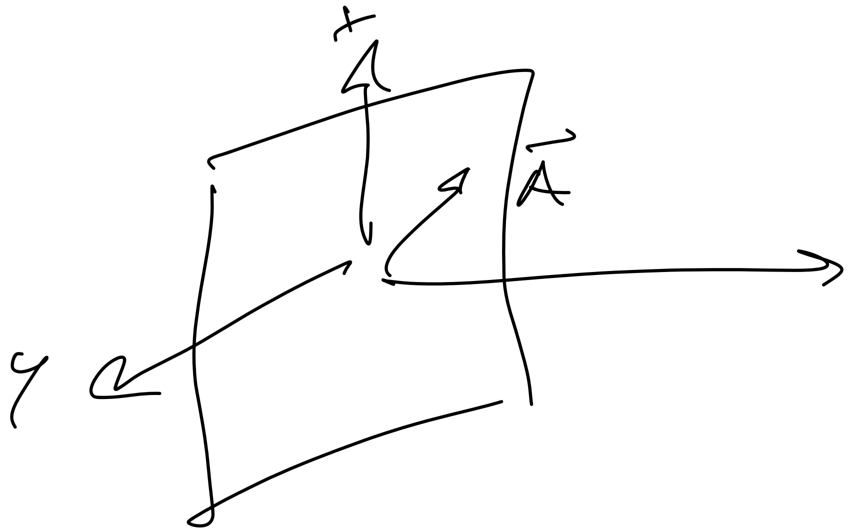
$\vec{\epsilon}$ vecteur de polarisation $\in \mathbb{C}^2$

$$|\vec{\epsilon}| = 1 \qquad \vec{\epsilon} = (\underbrace{\alpha_x}_{\in \mathbb{R}} e^{i\phi_x}, \underbrace{\alpha_y}_{\in \mathbb{R}} e^{i\phi_y})$$

$$\vec{E}(\vec{r},t) = -\frac{\partial \vec{A}}{\partial t} = \frac{A_0\omega}{2}\left[-i\vec{\epsilon}\, e^{i(\vec{k}\cdot\vec{r}-\omega t)} + c.c.\right]$$

$$\vec{B}(\vec{r},t) = \vec{\nabla}\times\vec{A} = \frac{A_0}{2}\left[i(\vec{k}\times\vec{\epsilon})\, e^{i(\vec{k}\cdot\vec{r}-\omega t)} + c.c.\right]$$

$$\vec{\nabla}\cdot\vec{A} = 0 \Longrightarrow \vec{k}\cdot\vec{\epsilon} = 0$$



$\vec{k} \perp \vec{E}$

$\vec{k} \parallel z$

Polarisation

$$\underline{\underline{\vec{A}}}(\vec{r},t) = A_0 \left[\cos(\underline{\underline{\vec{k}\cdot\vec{r}-\omega t + \phi_x}}) \, \alpha_x \vec{e}_x \right.$$

$$\left. + \cos(\vec{k}\cdot\vec{r}-\omega t + \underline{\underline{\phi_y}}) \, \alpha_y \, \vec{e}_y \right]$$

Cas remarquables :

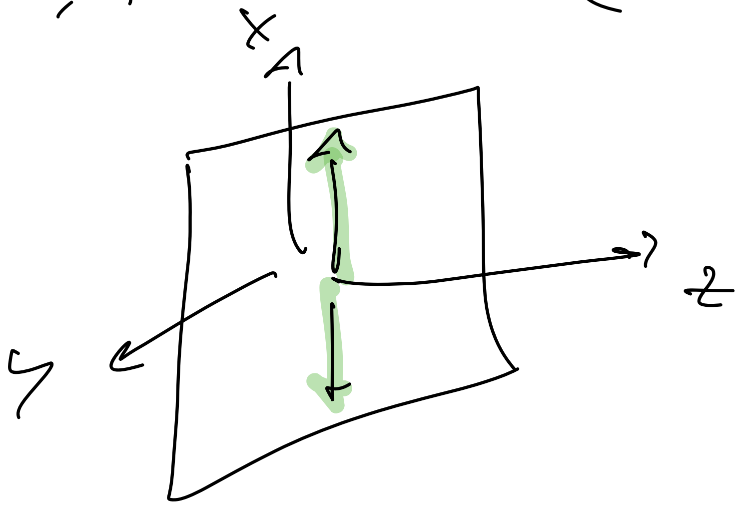
1) Polarisation linéaire

p.e. $\alpha_x = 1$ $\qquad \phi_x = 0$

$\alpha_y = 0$

$$\alpha_x^2 + \alpha_y^2 = 1$$

$$\vec{A}(\vec{r},t) = A_0 \cos(\vec{k}\cdot\vec{r} - \omega t)\, \vec{e}_x$$

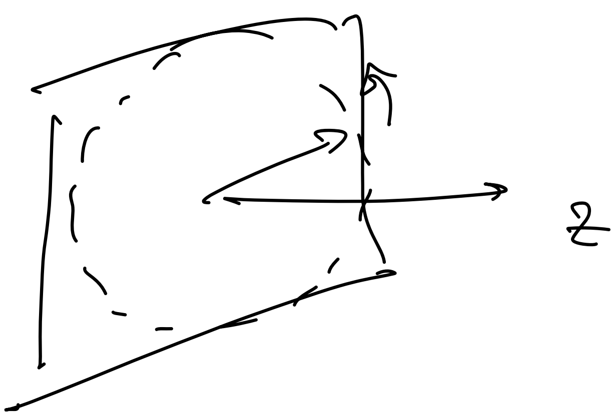


polarisation verticale

2) <u>Polarisation circulaire</u> (R) droite

$$\alpha_x = \alpha_y = \frac{1}{\sqrt{2}} \qquad \phi_x = 0 \qquad \phi_y = \frac{\pi}{2}$$

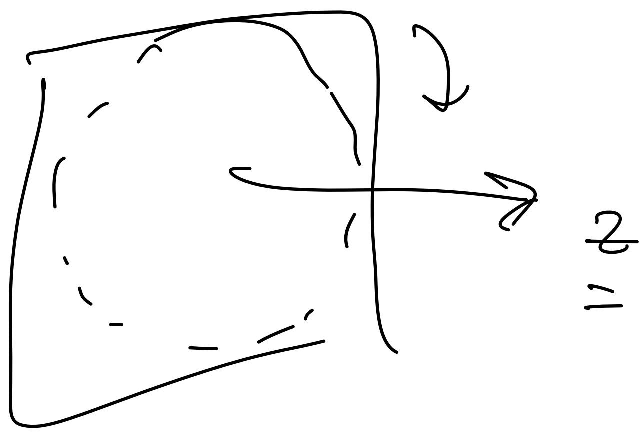
$$\vec{A}(\vec{r},t) = \frac{A_0}{\sqrt{2}} \left[\cos(\vec{k}\cdot\vec{r} - \omega t)\, \vec{e}_x - \sin(\vec{k}\cdot\vec{r} - \omega t)\, \vec{e}_y \right]$$



pol. circulaire droite (R)

3) Pol. circulaire (L) gauche

$\Phi_x = 0 \qquad \Phi_y = -\pi/2$



Base sphérique de l'espace $\mathbb{R}^3$

$\vec{e}_x, \vec{e}_y, \vec{e}_z \longrightarrow \vec{u}_0, \vec{u}_1, \vec{u}_{-1}$

$$\begin{cases} \vec{u}_0 = \vec{e}_z \\ \vec{u}_1 = \dfrac{\vec{e}_x + i\vec{e}_y}{\sqrt{2}} \\ \vec{u}_{-1} = \dfrac{\vec{e}_x - i\vec{e}_y}{\sqrt{2}} \end{cases}$$

$\vec{\epsilon} = \vec{u}_0$ linéaire (π)

$\vec{\epsilon} = \vec{u}_1$ circulaire droite (R) (σ^+)

$\vec{\epsilon} = \vec{u}_{-1}$ circulaire gauche (L) (σ^-)

Densité d'énergie moyenne associée au champ e.m.

$$\rho(\omega) = \frac{1}{2}\epsilon_0 \overline{|\vec{E}|^2} + \frac{1}{2}\frac{\overline{|\vec{B}|^2}}{\mu_0}$$

$$\epsilon_0\mu_0 = \frac{1}{c^2}$$

$$= \frac{1}{2}\epsilon_0 \left[\overline{|\vec{E}|^2} + c^2\,\overline{|\vec{B}|^2}\right]$$

$$= \dots = \frac{1}{2}\epsilon_0 A_0^2 \omega^2$$

onde monochromatique

$\vec{k}$, ω, $\vec{E}$

$\omega = ck$

$$A_0 = \sqrt{\frac{2\rho(\omega)}{\omega^2\epsilon_0}} = \sqrt{\frac{2\hbar\, n(\omega)}{\omega\,\epsilon_0\, V}}$$

$$\rho(\omega) = \frac{\hbar\omega\, n(\omega)}{V}$$

$$E_0 = A_0\omega = \sqrt{\frac{2\hbar\omega\, n(\omega)}{\epsilon_0 V}}$$

Interaction champ e.m. / atome

$$\mathcal{H} = \frac{\vec{p}^{\,2}}{2m} \qquad \vec{A},\ \phi \qquad \overrightarrow{\ q=-e\ } \qquad \frac{(\vec{p}+e\vec{A})^2}{2m} \cancel{- e\phi} \xrightarrow{} 0$$

$m \to \mu$

$$\hat{\mathcal{H}}_{at+champ} = \frac{(\hat{\vec{p}}+e\hat{\vec{A}})^2}{2m} - \frac{Ze^2}{4\pi\varepsilon_0 \hat{r}} + \dots$$

$2\vec{A}\cdot\vec{p}$

$$= \underbrace{\left(\frac{\hat{p}^2}{2m} - \frac{Ze^2}{4\pi\varepsilon_0 \hat{r}} + \dots\right)}_{\mathcal{H}_0} + \frac{e}{2m}\left(\hat{\vec{p}}\cdot\hat{\vec{A}} + \hat{\vec{A}}\cdot\hat{\vec{p}}\right) + \frac{e^2}{2m}\vec{A}^2$$

$$(\hat{\vec{p}}\cdot\hat{\vec{A}})\,\psi(\vec{r}) = (-i\hbar\vec{\nabla})\cdot(\vec{A}\psi)$$

$$= -i\hbar\left\{\cancel{(\vec{\nabla}\cdot\vec{A})}\,\psi + \vec{A}\cdot\vec{\nabla}\psi\right\} \qquad \cancel{(\vec{\nabla}\cdot\vec{A})} \to 0$$

$$= (\vec{A}\cdot\vec{p})\,\psi$$

$$\mathcal{H} = \mathcal{H}_0 + \underbrace{\frac{e}{m}\vec{A}^{(\vec r,t)}\cdot\vec{p} + \cancel{\frac{e^2A^2(\vec r,t)}{2m}}}_{\mathcal{H}'(t)}$$

$$\vec{A}(\vec r,t) = \frac{A_0}{2}\left[\vec{\epsilon}\, e^{i(\vec k\cdot\vec r-\omega t)} + c.c.\right]$$

$$\vec{A}^2 \sim \cos^2(\cancel{\vec k\cdot\vec r}-\omega t) \qquad \boxed{\vec k,\ \omega,\ \vec\epsilon}$$

$$k = \frac{2\pi}{\lambda} \qquad r \sim a_0 = 0.5\times10^{-10}$$

$$\lambda \simeq 100\ \mathrm{nm} = 10^{-7}\ \mathrm{m}$$

$$kr \simeq 10^{-3}$$

$$i\hbar\frac{\partial}{\partial t}\psi(\vec r,t) = \left[\mathcal{H}_0 + \mathcal{H}'(t)\right]\psi(\vec r,t)$$

Théorie des perturbations dépendante du temps

$$H_0 \psi_n = E_n \psi_n$$

$$\psi(\vec{r},t) = \sum_n c_n(t)\, e^{-\frac{i}{\hbar}E_n t}\, \psi_n(\vec{r})$$

$$\int d^3r\; i\hbar \sum_n \left(\dot{c}_n - \frac{i}{\hbar}E_n c_n\right) e^{-\frac{i}{\hbar}E_n t}\, \psi_n\, \psi_m^*$$

$$= \int d^3r \sum_n c_n\, e^{-\frac{i}{\hbar}E_n t} \left(E_n + H' \right) \psi_n\, \psi_m^*$$

$$\dot{c}_m = \frac{1}{i\hbar} \sum_n c_n \langle \psi_m | H'(t) | \psi_n \rangle\, e^{-\frac{i}{\hbar}(E_n - E_m)t}$$

$$\omega_{nm} = \frac{E_n - E_m}{\hbar} \qquad e^{i\omega_{nm} t}$$

$$\dot{c}_m = \frac{1}{i\hbar} \sum_n c_n \langle \psi_m | \mathcal{H}'(t) | \psi_n \rangle e^{i\omega_{mn} t}$$

$$\frac{e}{m} \vec{p} \cdot \vec{A}(\vec{r},t)$$

$$= \frac{e A_0}{2 i \hbar m} \sum_n c_n \Big[\underbrace{\langle \psi_m | \vec{\epsilon} \cdot \vec{p}\, e^{i(\vec{k}\cdot\vec{r})} | \psi_n \rangle}_{M_{mn}} e^{i(\omega_{mn}-\omega)t}$$

$$+ \underbrace{\langle \psi_m | \vec{\epsilon}^{\,*} \cdot \vec{p}\, e^{-i\vec{k}\cdot\vec{r}} | \psi_n \rangle}_{M^*_{nm}} e^{i(\omega_{mn}+\omega)t} \Big]$$

$$\dot{c}_m = \frac{e A_0}{2 i \hbar m} \sum_n c_n \left[M_{mn} e^{i(\omega_{mn}-\omega)t} + M^*_{nm} e^{i(\omega_{mn}+\omega)t} \right]$$

théorie des perturbations

$$\mathcal{H}' \to \lambda \mathcal{H}'$$

$$c_m(t) = c_m^{(0)} + \lambda c_m^{(1)}(t) + \lambda^2 c_m^{(2)}(t) + \dots$$

$$\dot{C}_m^{(1)} = \frac{eA_0}{2i\hbar m} \sum_n C_n^{(0)} \left[M_{mn}\, e^{i(\omega_{mn}-\omega)t} + M^*_{nm}\, e^{i(\omega_{mn}+\omega)t} \right]$$

T

conditions initiales

$$C_n^{(0)} = \delta_{k,n}$$

état initial est

$$\psi(\vec{r},0) = \underline{\underline{\psi_k}}(\vec{r},0)$$

$$\int_0^t dt' \, \dot{C}_m^{(1)} = \int_0^t dt' \frac{eA_0}{2i\hbar m} \left[M_{mk}\, e^{i(\omega_{mk}-\omega)t'} + M^*_{km}\, e^{i(\omega_{mk}+\omega)t'} \right]$$

$m \neq k$

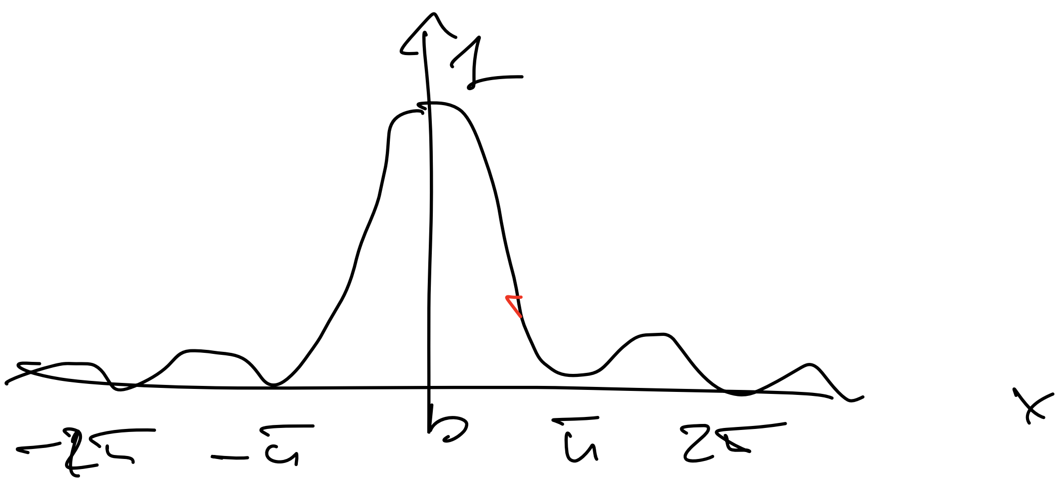
$$C_m^{(1)}(t) - \cancel{C_m^{(1)}(0)}^{\,0}$$

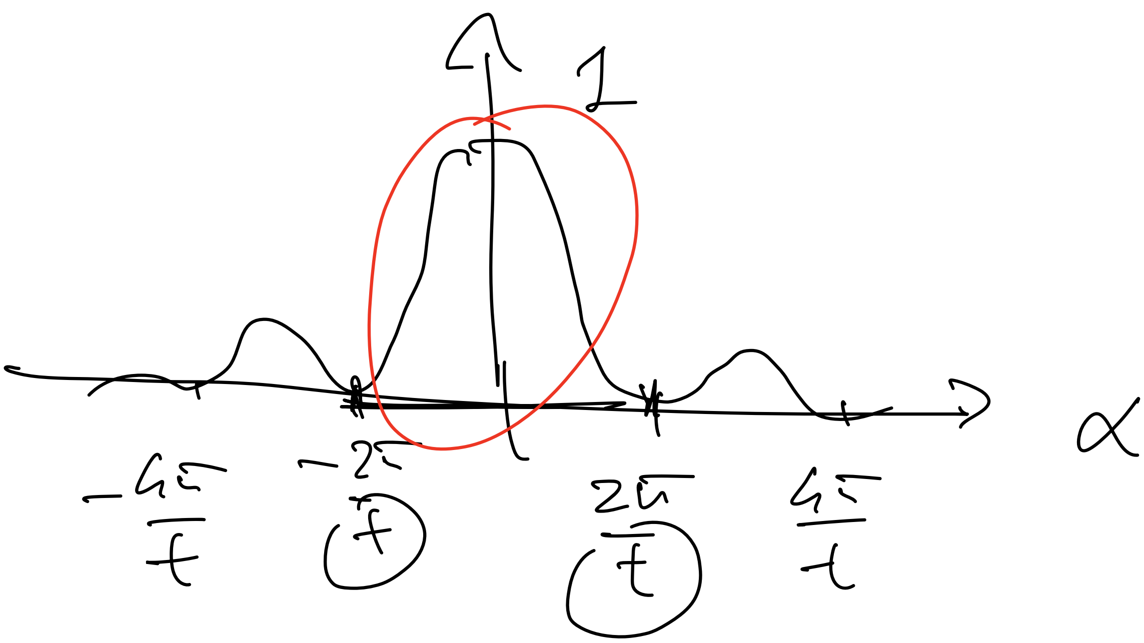
$$= \frac{eA_0}{2i\hbar m} \left[M_{mk} \frac{e^{i(\omega_{mk}-\omega)t} - 1}{i(\omega_{mk}-\omega)} \right.$$

$$+ M^*_{km} \frac{e^{i(\omega_{mn}+\omega)t}-1}{i(\omega_{mn}+\omega)} \Bigg]$$

$$\left|\frac{e^{i\alpha t}-1}{\cancel{i}\alpha}\right|^2 = t^2 \operatorname{sinc}^2\left(\frac{\alpha t}{2}\right)$$

$$\operatorname{sinc}^2(x) = \left(\frac{\sin x}{x}\right)^2$$





$$\int_{+\infty}^{+\infty} dx \; \mathrm{sinc}^2(x) = \pi$$

$$\int_{-\infty}^{+\infty} d\alpha \; \frac{t}{2} \; \mathrm{sinc}^2\left(\frac{\alpha t}{2}\right) = 2t\pi$$

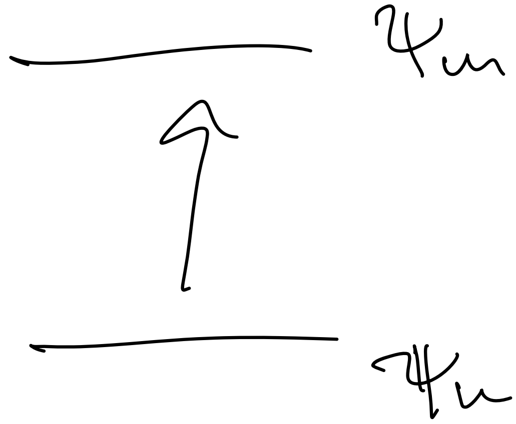
$$t \to \infty \qquad \frac{\sin^2\left(\frac{\alpha t}{2}\right)}{\left(\alpha/2\right)^2} = t^2 \, \mathrm{sinc}^2\left(\frac{\alpha t}{2}\right)$$

$$\longrightarrow 2t\pi \, \delta(\alpha)$$

$$t \to \infty \qquad \left| \frac{e^{i(\omega_{mn} \pm \omega)t} - 1}{i(\omega_{mn} \pm \omega)} \right|^2$$

$$\longrightarrow 2t\pi \, \delta(\omega_{mn} \pm \omega)$$

$$\propto \omega \simeq \omega_{mk} = \frac{E_m - E_n}{\hbar}$$



ABSORPTION

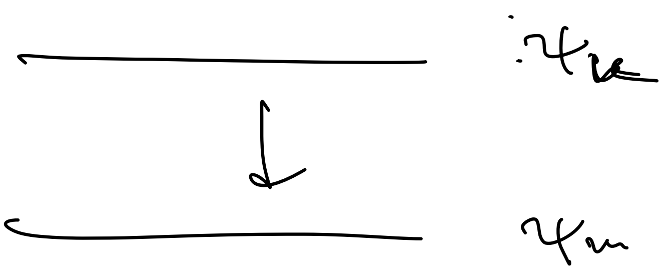
$$|C_m^{(1)}(t)|^2 \underset{t\to\infty}{=} \left|\frac{eA_0}{2i\hbar m}\right|^2 |M_{mn}|^2\, 2t\pi\, \delta(\omega_{mn} - \omega)$$

$$\Gamma_{n\to m} = \frac{|C_m^{(1)}|^2}{t} = \left(\frac{eA_0}{2\hbar m}\right)^2 |M_{mn}|^2\, 2\pi\, \delta(\omega - \omega_{mn})$$

taux de transition

EMISSION

$\omega_{mn} < 0$



$$\Gamma_{k \to m} = \left(\frac{eA_0}{2\hbar m}\right)^2 |M_{mk}|^2 \, 2\pi \, \delta(\omega + \omega_{mk})$$