Corrections relativistes à la physique de l'atome d'hydrogène

$$\frac{v}{c} \sim \alpha \simeq \frac{1}{137}$$ constante de structure fine

$$\hat{H} = \underline{\underline{\hat{H}_0}} + \underbrace{\hat{H}_{so} + \hat{H}_{rc} + \hat{H}_{D}}_{\sim o(\alpha^2)}$$

$\hat{H}_0$: $E_n = -\frac{Ry}{n^2}$

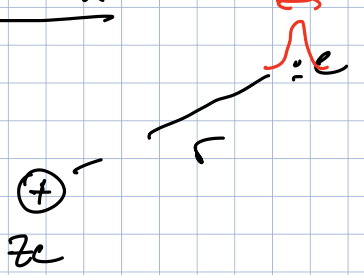
$\hat{H}_{so}$: interaction spin-orbite

$\hat{H}_{rc}$: correction relativiste à l'énergie cinétique

$\hat{H}_{D}$: terme de Darwin

Terme de Darwin

$$\lambda_c = \frac{\hbar}{mc}$$



$$[\hat{H}_D, \hat{L}^2] = [\hat{H}_D, \hat{L}_z] = 0$$

$\Downarrow$

$$V(\vec{r}) = -\frac{Ze^2}{4\pi\epsilon_0 r} + \underbrace{\frac{\pi\hbar^2}{2m^2c^2}\left(\frac{Ze^2}{4\pi\epsilon_0}\right)\underline{\underline{\delta(\vec{r})}}}_{\hat{H}_D} + \dots$$

$$\Delta E^{(D)}_{nl} = \langle nlm|\hat{H}_D|nl'm'\rangle \, \delta_{ll'}\,\delta_{mm'}$$

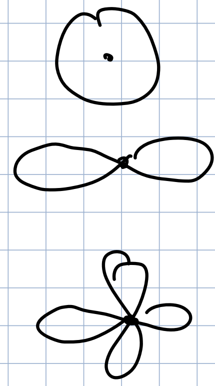
$$= \frac{\pi\hbar^2}{2m^2c^2}\left(\frac{Ze^2}{4\pi\epsilon_0}\right) \underbrace{\int_0^{\pi} d\theta \sin\theta \int_0^{2\pi} d\phi \, |Y_{lm}(\theta,\phi)|^2}_{1}$$

$$\int_0^{\infty} dr \, r^2 R_{nl}(r) \quad \delta(\vec{r})$$

$(^{*} \delta(r))$

$$= \frac{\pi\hbar^2}{2m^2c^2}\left(\frac{Ze^2}{4\pi\epsilon_0}\right) \int dx\,dy\,dz \, |\psi_{nlm}(x,y,z)|^2 \, \delta(x)\delta(y)\delta(z)$$

$$= \frac{\pi\hbar^2}{2m^2c^2}\left(\frac{Ze^2}{4\pi\epsilon_0}\right) \underbrace{|\psi_{nlm}(0)|^2}_{\delta_{l0}\,|\psi_{n00}(0)|^2}$$



$$\downarrow$$

$$\frac{Z^3}{\pi n^3 a_0^3}$$

$$= \dots = -E_n \frac{Z^4\alpha^2}{n}\,\delta_{l0} = \Delta E^{(D)}_{nl} \qquad 1$$

Interaction spin-orbite

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

Corr. rel. à l'énergie cinétique

$$3 \qquad \Delta E^{(rel)}_{nl} = -E_n\,\frac{Z^4\alpha^2}{n^2}\left(\frac{3}{4} - \frac{n}{l+\frac{1}{2}}\right)$$

$$\vec{J} = \vec{L} + \vec{S}$$

$$|nlm\rangle\,|s\,m_s\rangle \qquad\qquad |n\,l\,s,\ j\,m_j\rangle$$

$$n \ \longrightarrow \qquad \vec{L}^2 \ \ \vec{S}^2 \ \ \vec{J}^2 \ \ J_z$$

$$E_{nljs} = E_n + \Delta E_{nljs} \qquad < 0$$

$$\downarrow$$

$$\underbrace{\frac{Z^4 E_n\,\alpha^2}{n^2}\left[\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right]} \qquad E_n < 0, \quad [\dots] > 0$$

< 0

$=$ indépendant de l

$n \geq \ell + 1$

$j = \begin{cases} |\ell - \frac{1}{2}| \\ \ell + \frac{1}{2} \end{cases} \leq \ell + \frac{1}{2}$

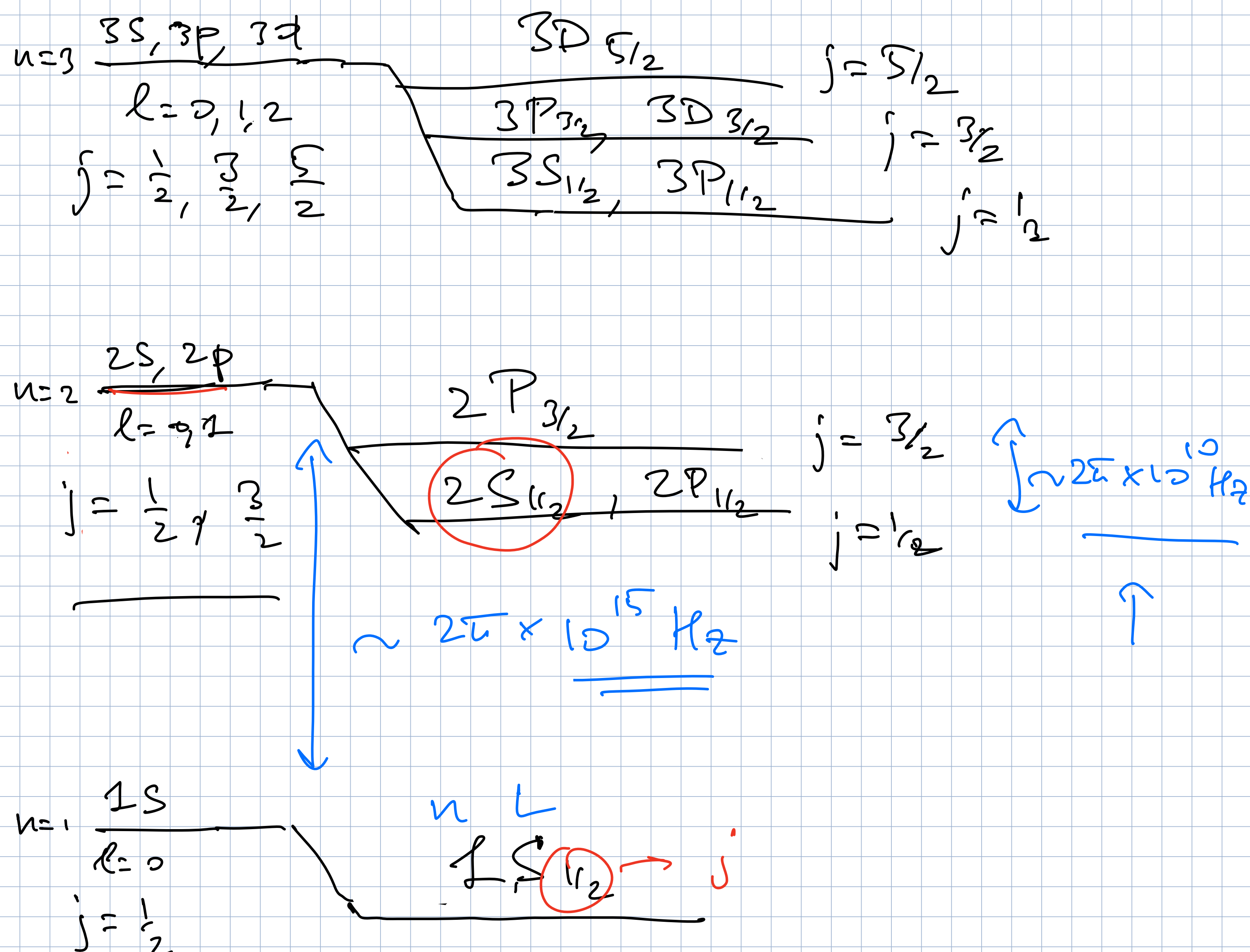
$n \geq \ell + 1 \geq j + \frac{1}{2}$

$j \leq \ell + 1$

$\dfrac{n}{j+\frac{1}{2}} \geq 1$

$j + \frac{1}{2} \leq \ell + 1$

Spectre "corrigé" de H : structure fine



"structure fine"

Base de la spectroscopie : interaction lumière - atome

Champ électromagnétique : objet classique

$$\begin{cases} \underline{\underline{\vec{E}}}(\vec{r},t) = -\dfrac{\partial \vec{A}}{\partial t}(\vec{r},t) - \vec{\nabla}\phi(\vec{r},t) \\ \underline{\underline{\vec{B}}}(\vec{r},t) = \vec{\nabla}\times\vec{A}(\vec{r},t) \end{cases}$$

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

$$\vec{\nabla}\cdot\vec{E} = \boxed{\frac{\rho}{\epsilon_0} = -\vec{\nabla}^2\phi} \longrightarrow \phi \sim \frac{1}{4\pi r} \quad \rho \sim \delta(\vec{r})$$

loin des charges ρ $\Rightarrow$ $\nabla^2\phi = 0$

solution $\boxed{\phi = 0}$

$\vec{A} \Rightarrow$ description complète de $\vec{E}$ et $\vec{B}$

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

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

$A_0 \in \mathbb{R}$ $\qquad \omega_{\vec{k}} = c|\vec{k}| = ck$

$\vec{\mathcal{E}}$ = polarisation $\qquad |\vec{\mathcal{E}}| = 1$

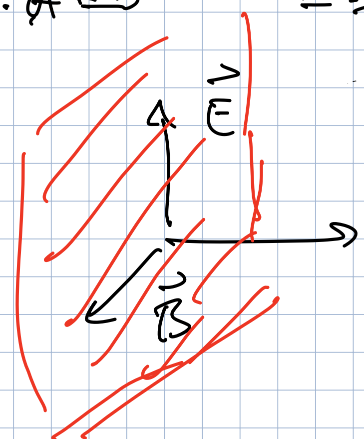
$\vec{\mathcal{E}} \in \mathbb{C}^2$

$\vec{\mathcal{E}} = (\alpha_x e^{i\phi_x}, \alpha_y e^{i\phi_y})$

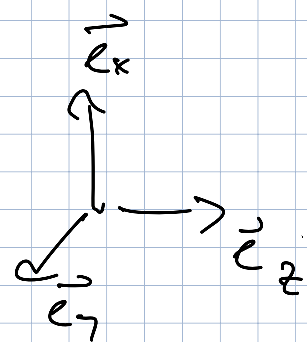
$\alpha_x, \alpha_y \in \mathbb{R}$

$$\begin{cases} \vec{E} = i\overbrace{\frac{A_0\omega}{2}}^{E_0}\,\underline{\underline{\vec{\mathcal{E}}}}\, e^{i(\vec{k}\cdot\vec{r}-ct)} + c.c. \\ \vec{B} = i\frac{A_0}{2}(\vec{k}\times\underline{\underline{\vec{\mathcal{E}}}})\, e^{i(\vec{k}\cdot\vec{r}-ct)} + c.c. \end{cases}$$

$\vec{\nabla}\cdot\vec{A} = 0 \Rightarrow \vec{k}\cdot\vec{\mathcal{E}} = 0$

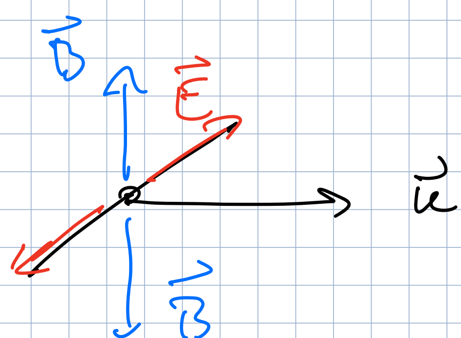


$\vec{k} \parallel z$



polarisations

1) $\vec{\mathcal{E}} = \vec{e}_x$ $\qquad$ polarisation linéaire

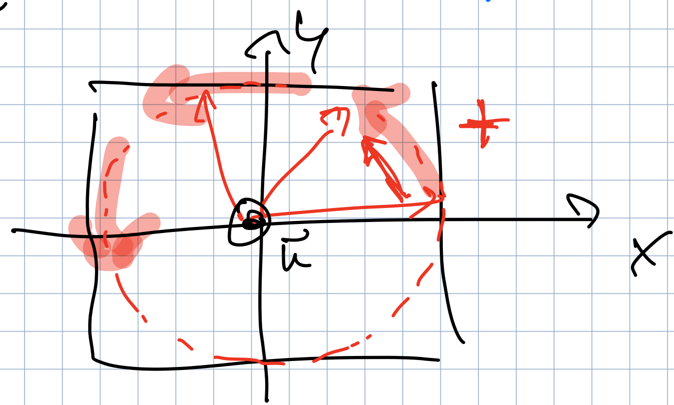


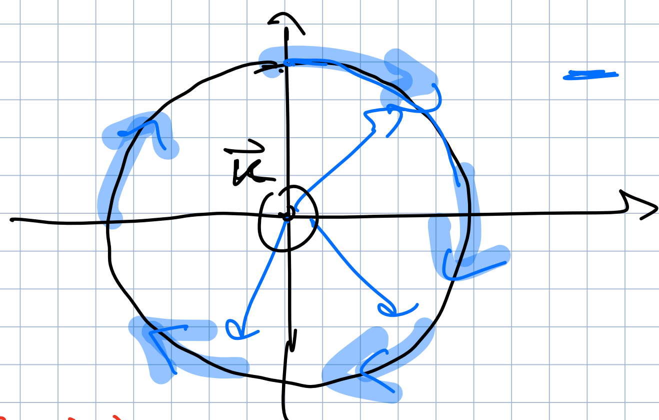
2) $\vec{E} = \dfrac{\vec{e}_x \pm i\,\vec{e}_y}{\sqrt{2}}$

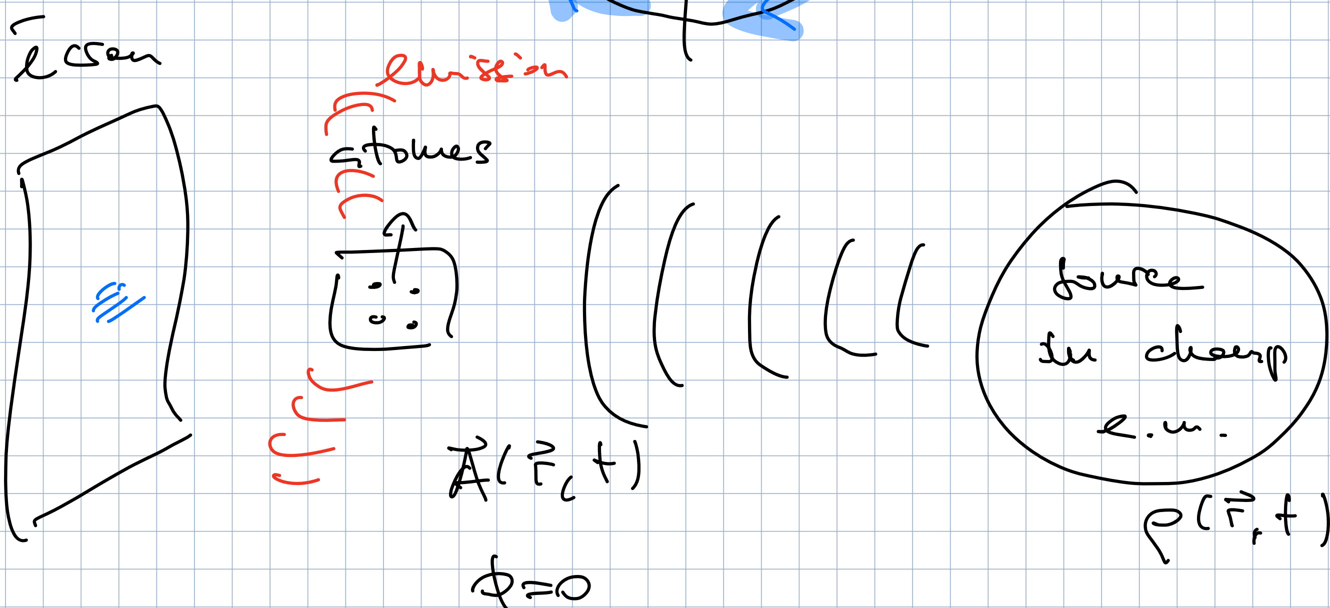
$+$ polarisation circulaire droite (R, σ^+)

$-$ " " gauche (L, σ^-)

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







base complexe : $\vec{e}_x, \vec{e}_y, \vec{e}_z$

$\rightarrow \quad \vec{u}_0 = \vec{e}_z$

base sphérique

$$\vec{u}_{\pm 1} = \frac{\vec{e}_x \pm i \vec{e}_y}{\sqrt{2}}$$

<u>Densité d'énergie associée au champ e.m.</u>

$$\rho(\omega) = \frac{1}{2} \varepsilon_0 \overline{|\vec{E}|^2} + \frac{1}{2} \frac{\overline{|\vec{B}|^2}}{\mu_0}$$

↓

énergie par unité de volume

$$= \frac{1}{2} \varepsilon_0 \left[\frac{A_0^2 \omega^2}{2} + c^2 A_0^2 \frac{|\vec{k} \times \vec{\varepsilon}|^2}{2} \right]$$

k^2

$$c^2 k^2 = \omega^2$$

$$= \frac{1}{2} A_0^2 \omega^2 \varepsilon_0$$

↑

$$A_0 = \sqrt{\frac{2\rho}{\omega^2 \varepsilon_0}}$$

$$E_0 = \omega A_0 = \sqrt{\frac{2\rho}{\varepsilon_0}} = \sqrt{\frac{2\hbar\omega\, n(\omega)}{\varepsilon_0 V}}$$

$$\rho = \frac{\hbar\omega \; n(\omega)}{V}$$ $n(\omega) \rightarrow$ # de photons

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Interaction lumière – atome (de H)

particule chargée $(-e)$ en présence de $\vec{A}$

$$\mathcal{H} = \frac{\vec{p}^{\,2}}{2m} - \frac{Ze^2}{4\pi\varepsilon_0 r} \rightarrow \hat{\mathcal{H}} = \frac{(\hat{\vec{p}} + e\hat{\vec{A}})^2}{2m} - \frac{Ze^2}{4\pi\varepsilon_0 r} \quad (\phi = 0)$$

$$= \frac{\hat{\vec{p}}^{\,2}}{2m} + \frac{e}{2m}\left(\hat{\vec{p}}\cdot\hat{\vec{A}} + \hat{\vec{A}}\cdot\hat{\vec{p}}\right) + \frac{e^2\vec{A}^2}{2m}$$

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

$h.c.$ → hermitian conjugé

→ $\vec{A}\cdot\vec{p} - \vec{p}\cdot\vec{A} = \ ?$

$$\underbrace{e^{-i\omega t}\, e^{i\vec{k}\cdot\hat{\vec{r}}}\,\vec{\varepsilon}\cdot\vec{p} - \vec{\varepsilon}\cdot\vec{p}\, e^{i\vec{k}\cdot\hat{\vec{r}}}\, e^{-i\omega t}}_{=0} + h.c. = 0$$

$\vec{\varepsilon}\cdot\vec{p} \perp \vec{k}\cdot\vec{r}$ $\qquad$ $\vec{\varepsilon} \perp \vec{k}$

↳ composantes orthogonales

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

négligeable

1) A est faible

2) $A^2 \simeq$ constant sur la taille de l'atome

$$\mathcal{H}'(t) = \frac{eA_0}{2m}\left(e^{i\vec{k}\cdot\vec{r}}\,\vec{p}\cdot\vec{\epsilon}\,e^{-i\omega t} + h.c.\right)$$

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

$\uparrow$ perturbation

$\lambda \ll 1$

$$\mathcal{H}_0\,\psi_n(\vec{r}) = E_n\,\psi_n(\vec{r})$$

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

$$\sum_n\left(i\hbar\,\dot{c}_n + \cancel{E_n c_n}\right)e^{-\frac{i}{\hbar}E_n t}\,\psi_n(\vec{r})$$

$$= \cancel{\sum_n c_n E_n e^{-\frac{i}{\hbar}E_n t}\psi_n} + \sum_n c_n e^{-\frac{i}{\hbar}E_n t}\,\underbrace{\mathcal{H}'(t)\,\psi_n(\vec{r})}$$

$$\int d^3r\,\psi_m^*(\vec{r})\,(\ldots) = \int d^3r\,\psi_m^*(\vec{r})\,(\ldots)$$

$$\int d^3r\,\psi_m^*\,\psi_n = \delta_{mn}$$

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

$$\int d^3r\,\psi_m^*\,\mathcal{H}'\,\psi_n$$

$$\frac{E_m - E_n}{\hbar} = \omega_{mn} = \omega_m - \omega_n$$

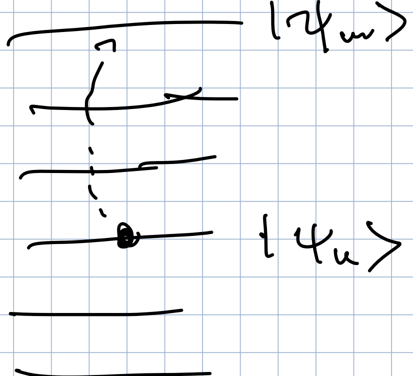
$$\dot{c}_m^{(t)} = \frac{eA_0}{2i\hbar m}\lambda \sum_n \underbrace{c_n^{(t)}}_{\delta_{n,k}} \Big[e^{i(\omega_{mn}-\omega)t} \underbrace{\langle \psi_m | e^{i\vec{k}\cdot\vec{r}} \vec{\epsilon}\cdot\vec{p} | \psi_n \rangle}_{M_{mn}} + e^{i(\omega_{mn}+\omega)t} \underbrace{\langle \psi_m | e^{-i\vec{k}\cdot\vec{r}} \vec{\epsilon}^{*}\cdot\vec{p} | \psi_n \rangle}_{M^{*}_{nm}} \Big]$$

conditions initiales

$$c_n(0) = \underline{\underline{\delta_{n,k}}} \qquad \text{état initial} \quad \underline{\psi(\vec{r}, t=0) = \psi_k(\vec{r})}$$

$$c_m(t) = \delta_{km} + \lambda c_m^{(1)}(t) + \underline{\underline{o(\lambda^2)}}$$

$$\dot{c}_m^{(1)} = \frac{eA_0}{2i\hbar m}\left(e^{i(\omega_{mk}-\omega)t} M_{mk} + e^{i(\omega_{mk}+\omega)t} M^{*}_{km} \right)$$



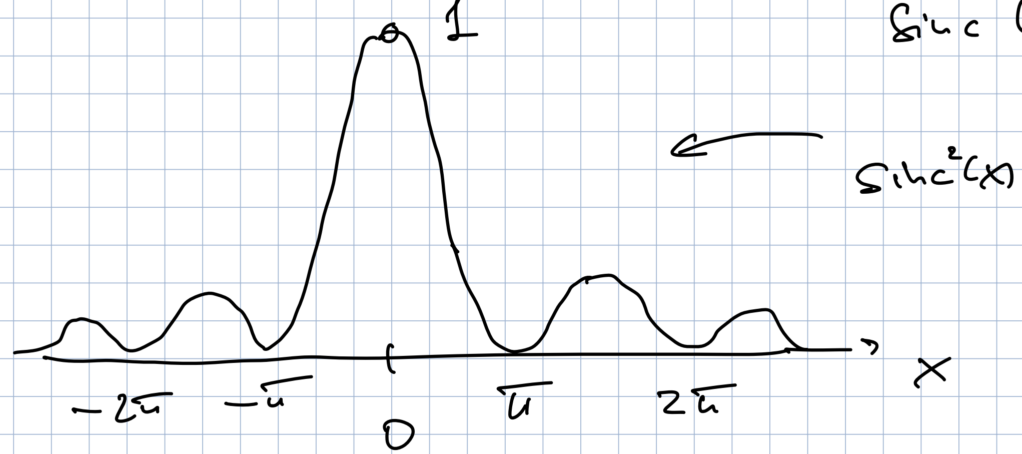
$$c_m^{(1)}(t) - \cancel{c^{(1)}(0)}^{\,0} = \frac{eA_0}{2i\hbar m}\left[\frac{e^{i(\omega_{mk}-\omega)t} - 1}{i(\omega_{mk}-\omega)} M_{mk} \right.$$

$m \neq k$

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

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

$$\mathrm{sinc}(x) = \frac{\sin(x)}{x}$$



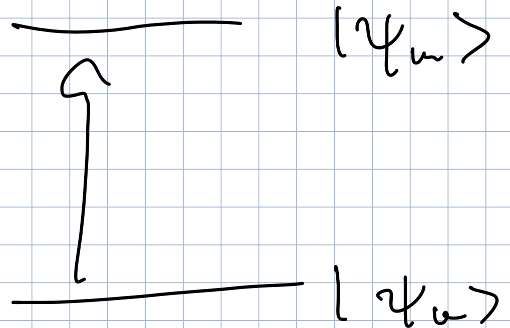
$\mathrm{sinc}^2\left(\frac{\alpha t}{2}\right)$

$$\left|\frac{e^{i\alpha t}-1}{\alpha}\right|^2 \xrightarrow[t\to\infty]{} 2\pi t\,\delta(\alpha)$$

$$\alpha = \omega_{mn} \pm \omega$$

Si $\omega_{mn} = \dfrac{E_m - E_n}{\hbar} \simeq \omega > 0$

$$\omega_{mn} - \omega \simeq 0$$



ABSORPTION

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

$\downarrow$

proba d'être en $|\psi_m\rangle$

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

taux de transition

règle d'or de Fermi