Interaction lumière - atome

$|m\rangle \quad E_m$

$\omega_{mk} \uparrow$

$|k\rangle \quad E_k$

$\vec{k}, \omega = ck, \vec{\varepsilon} \qquad \omega \simeq \omega_{mk}$

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

$$\Gamma_{k\to m} = \frac{2\pi}{\hbar^2}\left|\frac{eA_0}{2m}\langle m|\,\underbrace{e^{i\vec{k}\cdot\vec{r}}\,\vec{\varepsilon}\cdot\underline{\vec{p}}}_{}\,|k\rangle\right|^2 \delta(\omega-\omega_{mk}) \leftarrow$$

$M_{mk} \neq 0$

$$\omega_{mk} = \frac{E_m - E_k}{\hbar}$$

$\neq 0$?

dépend de $|k\rangle, |m\rangle, \vec{\varepsilon}$

"Approximation de dipole électrique"

$k \sim \frac{2\pi}{\lambda}$ $\qquad \lambda \simeq 500$ nm $\qquad$ spectre visible

$r \sim 1$ Å $\qquad \underline{\underline{H}}$ $\qquad \omega = \frac{2\pi}{\lambda}c$

$kr \sim 10^{-3}$

$e^{i\vec{k}\cdot\vec{r}} \sim 1 \Leftarrow + i\vec{k}\cdot\vec{r} + \ldots$

$n=3$

$n=2$ $\qquad \lambda \simeq 600$ nm

$(\lambda \simeq 160$ nm$)$

$n=1$

But : déterminer les conditions sur $|k\rangle, |m\rangle$ et $\vec{\varepsilon}$ pour que

$$|\langle m|\vec{\varepsilon}\cdot\hat{\vec{p}}|k\rangle|^2 \neq 0$$

règles de sélection (en approx. de dipole)

Équation de Heisenberg : $\qquad \hat{\vec{r}} = \hat{\vec{r}}(t)$

$$i\hbar\frac{d\hat{\vec{r}}}{dt} = [\hat{\vec{r}}, \hat{H}]$$

$$i\hbar \frac{d\hat{x}}{dt} = [\hat{x}, \hat{\mathcal{H}}_0] \qquad \hat{\mathcal{H}}_0 = \underbrace{\frac{\hat{\vec{p}}^2}{2m}}_{T} + \dots$$

$$= \left[\hat{x}, \frac{\hat{p}_x^2}{2m}\right]$$

$$= \frac{1}{2m}\Big(\underbrace{[\hat{x}, \hat{p}_x]}_{i\hbar}\hat{p}_x + \hat{p}_x\underbrace{[\hat{x}, \hat{p}_x]}_{i\hbar}\Big)$$

$$= \frac{i\hbar}{m}\hat{p}_x \implies \hat{p}_x = m\frac{d\hat{x}}{dt}$$

$$\hat{\vec{p}} = \frac{m}{i\hbar}[\hat{\vec{r}}, \hat{\mathcal{H}}_0] \leftarrow$$

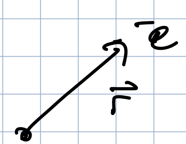
$$\vec{\varepsilon}\cdot\langle m|\hat{\vec{p}}|n\rangle = \frac{m\vec{\varepsilon}}{i\hbar}\langle m|(\hat{\vec{r}}\overbrace{\hat{\mathcal{H}}_0}^{E_n} - \underbrace{\hat{\mathcal{H}}_0}_{E_m}\hat{\vec{r}})|n\rangle$$

$$= \frac{m}{i\hbar}\underbrace{(E_n - E_m)}_{i\omega_{mn}}\langle m|\vec{\varepsilon}\cdot\hat{\vec{r}}|n\rangle$$

$$= i\omega_{mn}\, m\, \langle m|\vec{\varepsilon}\cdot\hat{\vec{r}}|n\rangle$$

$$\hat{\vec{d}} = -e\hat{\vec{r}}$$

dipole électrique de H



approx. de dipole électrique

$$\Gamma_{m\to n} \hat{=} \frac{2\pi}{\hbar^2}\left(\frac{\cancel{e}A_0}{2\cancel{m}c}\right)^2 \underset{\omega^2}{\underset{\downarrow}{\omega_{mn}^2}} \cancel{m^2}\, |\langle m|\vec{\varepsilon}\cdot\hat{\vec{d}}|n\rangle|^2\, \delta(\omega-\omega_{mn})$$

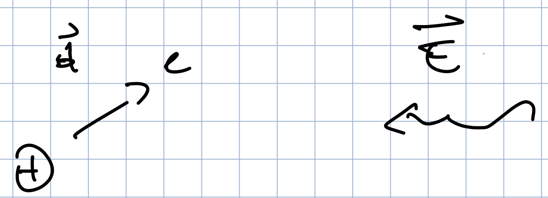
$$= \frac{2\pi}{\hbar^2}\left|\langle m|\Big(-\frac{\overbrace{A_0\omega}^{E_0}}{2}\vec{\varepsilon}\cdot\vec{d}\Big)|n\rangle\right|^2 \delta(\omega-\omega_{mn})$$

$$= \frac{2\pi}{\hbar^2}|\langle m|\hat{V}|n\rangle|^2\, \delta(\omega-\omega_{mn})$$

$$H(t) = H_0 + \left(\hat{V} e^{-i\omega t} + h.c.\right)$$

$$= H_0 - \underbrace{\left(\frac{\mathcal{E}_0}{2} e^{-i\omega t}\, \vec{\epsilon} + h.c.\right)}_{\vec{E}(t)} \cdot \vec{d}$$

$$= H_0 - \vec{E}(t) \cdot \vec{d}$$



Règles de sélection en approx. de dipole électrique

$$\langle m | \vec{\epsilon} \cdot \underset{(e\vec{r})}{\vec{d}} | n \rangle \neq 0$$

atome de H

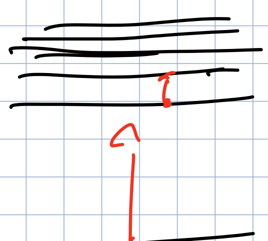
$$\vec{L}^2 \quad \vec{S}^2 \quad \vec{J}^2 \quad J_z$$

$$-e \underbrace{\langle n' l' s;\, j' m_j' | \vec{\epsilon} \cdot \vec{r} | n l s;\, j m_j \rangle}$$

$$\begin{cases} \Delta n = n' - n \\ \Delta l = l' - l \\ \Delta j = j' - j \\ \Delta m_j = m_j' - m_j \end{cases}$$

?

pour quelles valeurs a-t-on $\langle \cdot | \vec{\epsilon} \cdot \vec{d} | \cdot \rangle \neq 0$?



$$\vec{\epsilon} \cdot \vec{r} = \epsilon_0 r_0 + \epsilon_1 r_1 + \epsilon_{-1} r_{-1}$$

pol. linéaire

→ pol. circ. droite

→ pol. circ. gauche

$$\sum_{q=0,\pm 1} |\epsilon_q|^2 = 1$$

$$\boxed{r_0 = z \qquad r_1 = \frac{x+iy}{\sqrt{2}} \qquad r_{-1} = \frac{x-iy}{\sqrt{2}}}$$

$$\langle \underbrace{n'\ell' s_i'}_{\gamma'}\, j' m_j' \,|\, r_q \,|\, \underbrace{n \ell s_i}_{\gamma}\, j m_j \rangle$$

$$\langle \gamma_i'\, j' m_j' \,|\, r_q \,|\, \gamma_i\, j m_j \rangle$$

Théorème de Wigner-Eckart

$$\begin{cases} z = r\cos\theta \\ x = r\sin\theta\cos\phi \\ y = r\sin\theta\sin\phi \end{cases}$$

$$\begin{cases} r_0 = r\cos\theta \\ r_1 = r\sin\theta\,\dfrac{\overbrace{\cos\phi + i\sin\phi}^{e^{i\phi}}}{\sqrt{2}} = r\sin\theta\,\dfrac{e^{i\phi}}{\sqrt{2}} \\ r_{-1} = r\sin\theta\,\dfrac{e^{-i\phi}}{\sqrt{2}} \end{cases}$$

$$Y_{10}(\vartheta,\phi) = \sqrt{\frac{3}{4\pi}}\cos\vartheta$$

$$Y_{1,\pm 1}(\vartheta,\phi) = \sqrt{\frac{3}{8\pi}}\sin\vartheta\, e^{\pm i\phi}$$

$Y_{\ell m}$

$\ell = 1$

&

$$r_q = \sqrt{\frac{4\pi}{3}}\, r\, Y_{1,q}(\vartheta,\phi)$$

$\hat{\vec{r}}$ opérateur vectoriel $\rightarrow$ $\hat{r}_q$

Théorème de Wigner–Eckart

pour des opérateurs vectoriels

$\vec{r}, \vec{F}, \vec{L}, \vec{S}, \vec{J}, \ldots$

&

opérateurs qui se transforment comme des vecteurs sous rotation

états propres d'opérateurs moment cinétique

$$\langle \gamma', j' m_j' | \hat{r}_q | \gamma, j m_j \rangle = \;?$$

idée :

$$\hat{r}_q | \gamma, j m_j \rangle \sim |1\; q\rangle \otimes |\gamma, j m_j\rangle$$

$\vec{J}^2, J^z$; $\vec{J}_1^2$, J_1^z ; $\vec{J}_2^2$, J_2^z

se comporte comme

ne dépend pas de q, m_j, m_j'

$$\langle \gamma', j' m_j' | \hat{r}_q | \gamma, j m_j \rangle = \underbrace{\langle \gamma' j' \| r \| \gamma j \rangle}_{\text{élément de matrice réduit}}\; C^{1\,j}_{q\, m_j;\, j' m_j'}$$

rappel

$$\langle j' m_j' | \left(|j_1 m_1\rangle |j_2 m_2\rangle \right) = C^{j_1 j_2}_{m_1 m_2 ; j' m_j'}$$

Théorème de Wigner-Eckart & règles de sélection

$$\boxed{\begin{cases} \Delta n = n' - n = \text{quelconque} \\ \Delta \ell = \ell' - \ell = \pm 1 \\ \Delta j = j' - j = 0, \pm 1 \\ \Delta m_j = m_j' - m_j = q \end{cases}}$$

$\Longleftarrow$ (photon a un moment cinétique intrinsèque $S=1$)

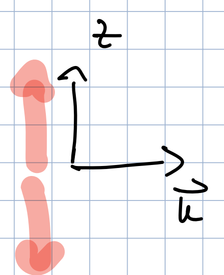
$$C^{1\, j}_{q m_j ; j' m_j'} \neq 0$$

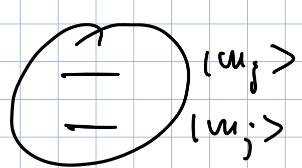
$$j' = |j-1|, j, j+1 = j, j \pm 1$$

$$m_j' = m_j + q$$

$$\sum_{q=0,\pm 1} \langle \gamma' ; j' m_j' | \epsilon_q r_q | \gamma ; j m_j \rangle$$

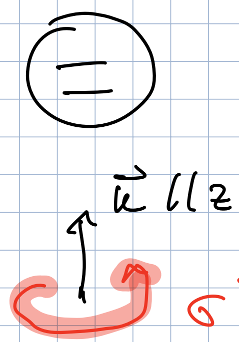
$\Delta m_j = 0 \qquad \epsilon_0 = 1$





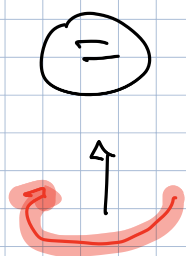
$\Delta m_j = 0$

$\underline{\underline{\Delta m_j = +1}}$ $\qquad \epsilon_1 = 1$



σ^+, R

$\Delta m_j = -1$ $\qquad \epsilon_{-1} = 1$



σ^-, L

$\boxed{\Delta l = \pm 1} \Leftarrow$

$$|nls;jm_j\rangle = \sum_{m m_s} C^{ls}_{m m_s; j m_j} |nlm\rangle |s m_s\rangle$$

$$\langle n'l's; j'm_j'| r_q | nls; jm_j\rangle$$

$$= \sum_{m m_s} \sum_{m' m_s'} C^{l's}_{m' m_s'; j' m_j'} C^{ls}_{m m_s; j m_j} \underbrace{(\langle n'l'm'| \langle s m_s'|) \hat{r}_q (|nlm\rangle |s m_s\rangle)}_{\delta_{m_s m_s'} \langle n'l'm'| r_q | nlm\rangle}$$

$$\langle n'\ell' m' | r_q | n\ell m\rangle \underset{W-E}{=} \langle n'\ell' \| r \| n\ell\rangle \, C^{1\ell}_{mq;\ell' m'}$$

$$\Delta \ell = \cancel{0}, \pm 1 \qquad \ell' = \ell-1, \ell, \ell+1$$

$$r_q = \sqrt{\frac{4\pi}{3}}\; r \; Y_{1q}(\theta, \phi)$$

$$\sqrt{\frac{4\pi}{3}} \int_0^\infty dr\, r^2 R^*_{n'\ell'}(r) R_{n\ell}(r)\, r \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi \; Y^*_{\ell' m'} Y_{1q} Y_{\ell m}$$

$$(-1)^{\ell'+1+\ell}$$

inversion de l'espace

$$Y_{\ell m}(\theta, \phi) \to (-1)^\ell Y_{\ell m}(\theta, \phi)$$

$$\theta \to \pi - \theta$$

$$\phi \to \phi + \pi$$

pour que ça soit finie :

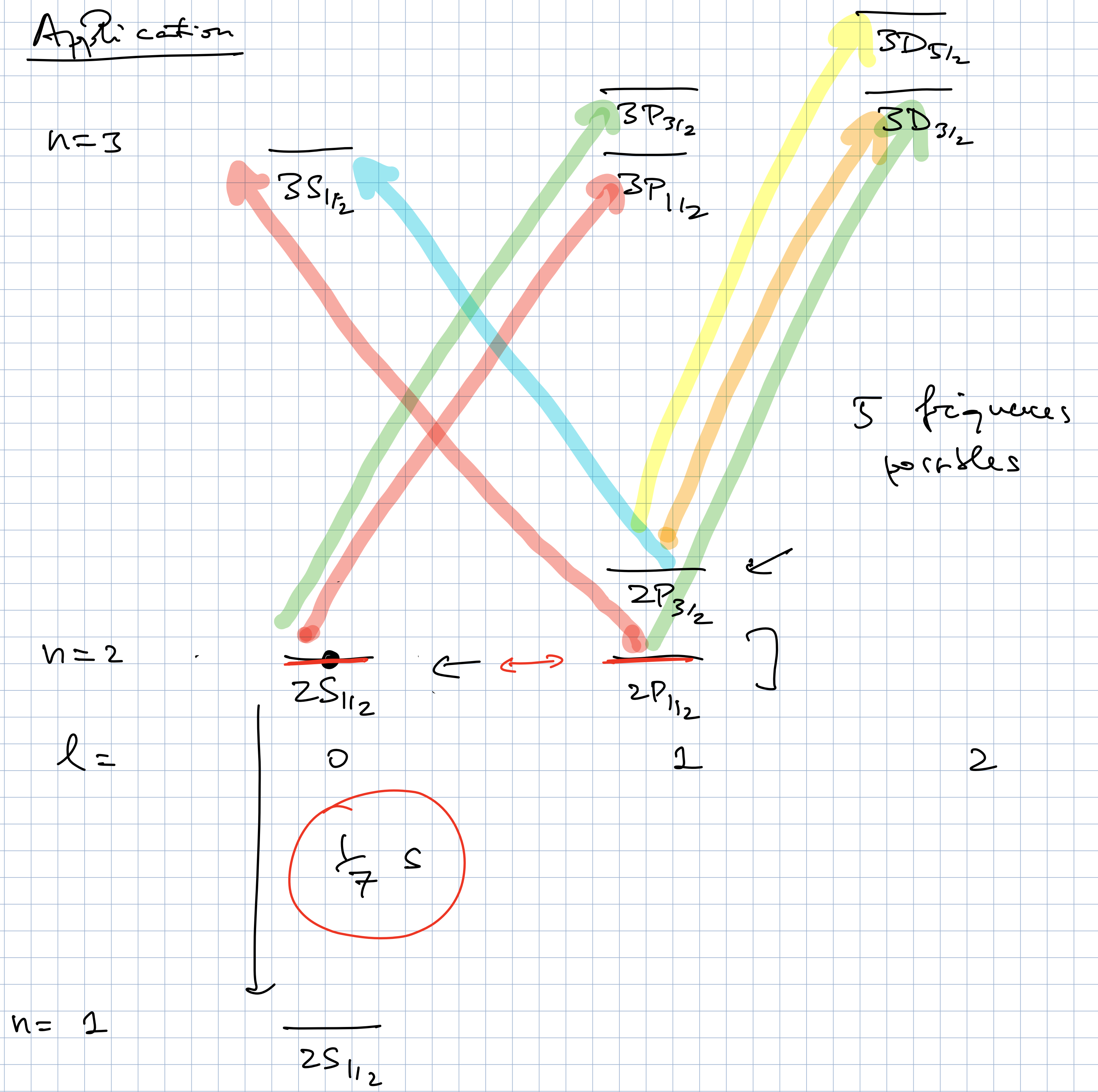
$$1 + \ell' + \ell = \text{pair}$$

$$\underline{\underline{\ell' + \ell}} = \text{impair}$$

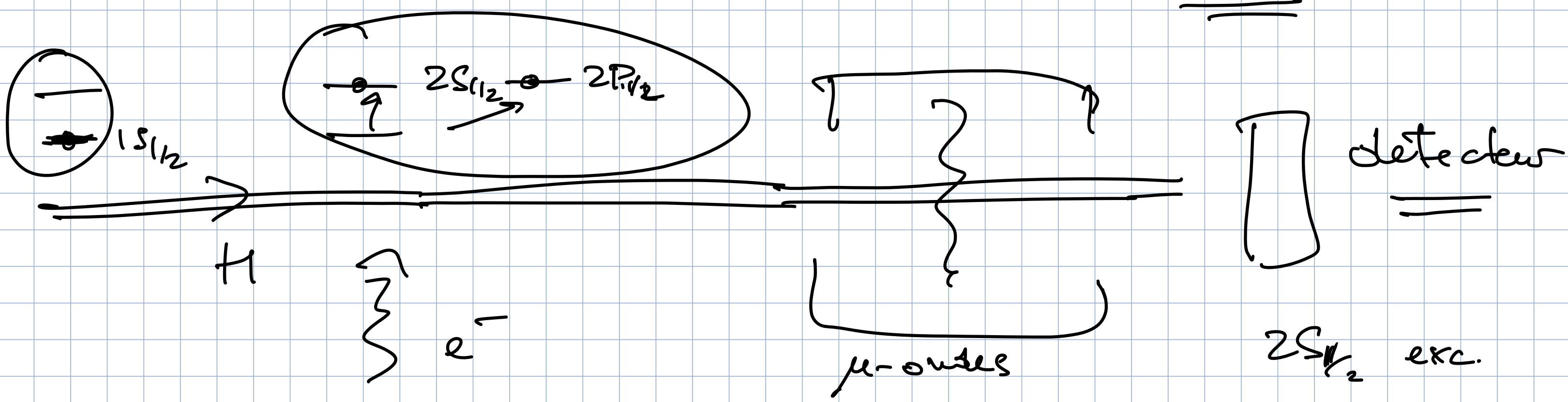
si $\Delta \ell = 0$ $\quad \ell + \ell' = \text{pair} = 2\ell$ $\quad \Rightarrow$ annulation de l'élément de matrice

$$\begin{cases} \Delta n = n' - n = \text{quelconque} \\ \Delta \ell = \ell' - \ell = \pm 1 \\ \Delta j = j' - j = 0, \pm 1 \\ \boxed{\Delta m_j = m_j' - m_j = q} \end{cases}$$

Application



Décalage de Lamb, Retherford (1947)



$2S_{1/2}$ exc.

$2P_{1/2} \to$ de-exc.