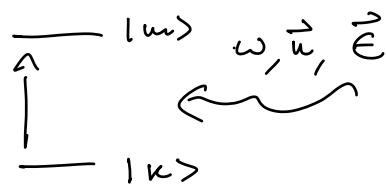


Interaction Raman - atomes

Absorption / émission troublée



$$H(t) = H_{\text{at}} + \left[\frac{e\vec{E}_0}{2m} \vec{p} + \vec{E} \cdot \vec{p} e^{i\vec{k} \cdot \vec{r}} + \text{h.c.} \right]$$

$$\Gamma_{n \rightarrow m} = \frac{2\pi}{\hbar^2} \left(\frac{e\vec{A}_0}{2m} \right)^2 \underbrace{\left| \langle m | \vec{E} \cdot \vec{p} e^{i\vec{k} \cdot \vec{r}} | n \rangle \right|^2}_{\omega_{mn} = \frac{\epsilon_m - \epsilon_n}{\hbar}} \delta(\omega - \omega_{mn})$$

$$M_{mn} \neq 0 ?$$

$M_{mn} \Rightarrow$ transition "interdite"

$M_{mn} \neq 0 \Leftrightarrow$ règles de sélection

Approximation de dipole (électrique)

$$\vec{k} \cdot \vec{r} \sim 10^{-3} \div 10^{-2} \approx 0$$

$$r \sim r_0 \sim 10^{-10} \text{ m}$$

$$k \sim \frac{2\pi}{\lambda} \quad \underline{2 \times 10^{-7} \text{ m}}$$

$$M_{mn} = \langle m | \vec{E} \cdot \vec{p} e^{i\vec{k} \cdot \vec{r}} | n \rangle \approx \vec{E} \cdot \underbrace{\langle m | \vec{p} | n \rangle}_{1}$$

$$\hat{H}_{\text{ext}} = \left(\frac{\vec{p}^2}{2m} + U_{\text{ext}} + \dots \right)$$

\rightarrow Effets propres
de \hat{H}_{ext}

$$\vec{s}_m = \vec{r}_m = \vec{r}$$

$$i\hbar \dot{\vec{r}} = [\vec{r}, \hat{H}_{\text{ext}}]$$

$$\left[\vec{x}, \frac{\vec{p}^2}{2m} \right] = \frac{i\hbar}{2m} \left[\vec{x}, p_x^2 + p_y^2 + p_z^2 \right]$$

$$\vec{x} = \frac{i\hbar}{m} \vec{p}_x$$

$$[\vec{r}, \hat{H}_{\text{ext}}] = \frac{i\hbar}{m} \vec{p}_r$$

$$\vec{p} = \frac{m}{i\hbar} [\vec{r}, \hat{H}_{\text{ext}}]$$

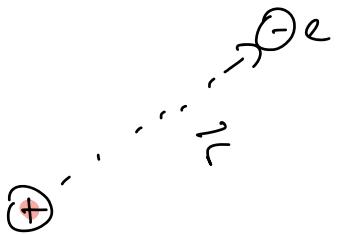
$$\langle u | \vec{p} | v \rangle = \frac{m}{i\hbar} \langle u | [\vec{r}, \hat{H}_{\text{ext}}] | v \rangle$$

$$\begin{aligned} & (\vec{r} \hat{H}_{\text{ext}} - \hat{H}_{\text{ext}} \vec{r}) \\ & \vec{E}_m \quad \vec{E}_n \end{aligned}$$

$$= \sum_{\vec{r}}^m (\epsilon_r - \epsilon_n) \langle u | \vec{r} | v \rangle$$

$$= i m \omega_{mn} \langle u | \vec{r} | v \rangle = \frac{i m \omega_{mn}}{e \vec{d}_{mn}}$$

$$\vec{d}_{mn} = \langle m | \vec{d} | n \rangle$$



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

$$\Gamma_{u \rightarrow m} \underset{\text{dipole}}{\approx} \frac{2\pi}{h^2} \left(\frac{e^2}{c^2 \mu} \right)^2 \frac{m}{\epsilon} \omega^2 |\vec{d}_{mn}|^2 \delta(\omega - \omega_{mn})$$

$$E_0 = A_0 \omega$$

$$\vec{E}(r,t) = \frac{\epsilon_0}{2} \left(e^{i(kr - \omega t)} \vec{E} + c.c. \right)$$

$$\Gamma_{u \rightarrow m} \approx \frac{2\pi}{h^2} \underbrace{\left(\frac{E_0}{2} \right)^2 |\vec{d}_{mn} \cdot \vec{E}|^2}_{\text{Interaction}} \delta(\omega - \omega_{mn})$$

$$H(t) = H_{at} + (\nabla e^{-ict} + h.c.)$$

$$\nabla = -\frac{\epsilon_0}{2} \vec{E} \cdot \vec{\nabla}$$

interaction

charge electric dipole

$$= H_{at} - \vec{E} \cdot \vec{d}$$

A hand-drawn diagram of an ellipse with a vertical arrow labeled \vec{d} pointing from the center towards the bottom-left side of the ellipse.

$$\langle u | \vec{d} \cdot \vec{e} | u \rangle = 0$$

Règles de sélection en approximation de dipole pour l'atome de H

$$\Rightarrow \langle u | \vec{d} \cdot \vec{e} | u \rangle \neq 0 ?$$

$$\begin{aligned} & \text{Not } \frac{1}{j^2} \\ & \langle n'l's; j^m_j | \vec{d} \cdot \vec{e} | n'l's; j^m_j \rangle \rightarrow j^2 \\ & \downarrow \quad \quad \quad \downarrow \\ & \langle u | \end{aligned}$$

$|u\rangle$

$$\left\{ \begin{array}{l} \Delta n = n' - n = \text{quelque } ? \\ \Delta j = j' - j = 0, \pm 1 \\ \Delta l = l' - l = \pm 1 \\ \Delta m_j = m_j' - m_j = q \\ \vec{e} = \vec{u}_q \end{array} \right.$$

pour quelles transitions ai-je $\langle u | \vec{d} \cdot \vec{e} | u \rangle \neq 0$?

Théorème de Wigner-Eckart

$$\langle n'l's; j^m_j | \rightarrow \langle l's; j^m_j | \vec{J}, j^2$$

opérateur vectoriel : $\vec{r}, \vec{p}, \vec{l} (\vec{j})$

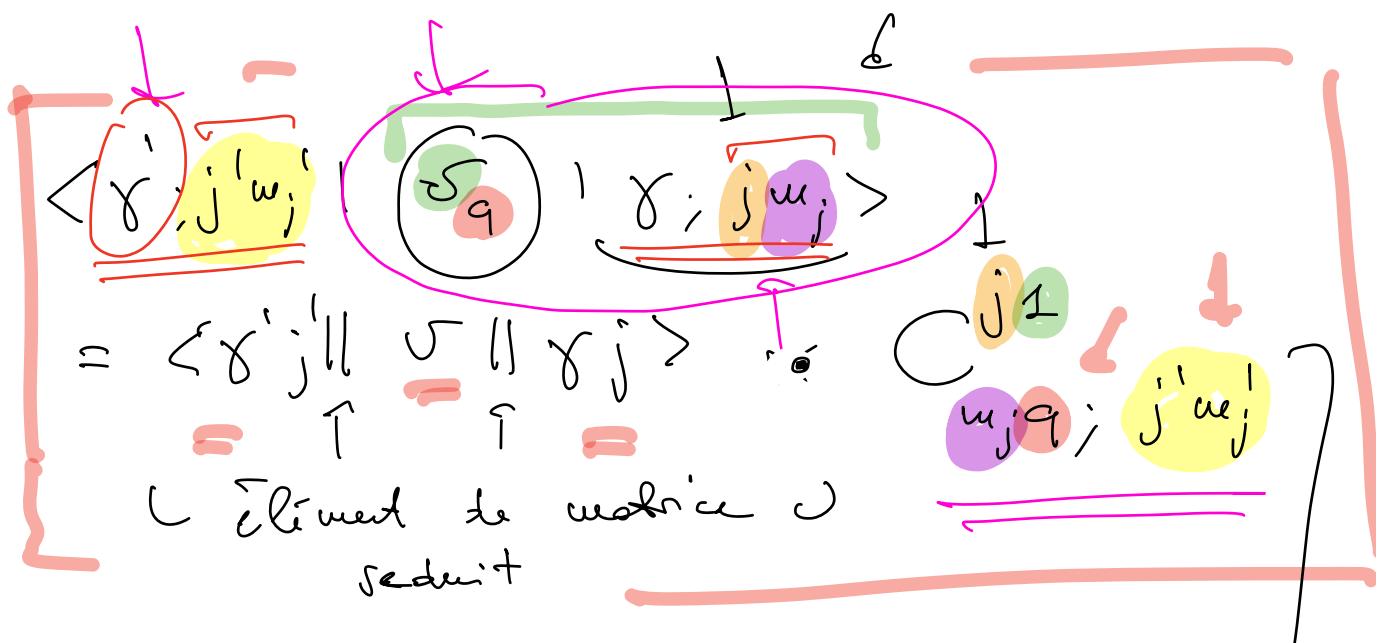
opérateur qui se transforme comme un vecteur sous les rotations engendrées par \vec{j}

$$U = e^{-i\theta \vec{r} \cdot \vec{j}}$$

en vecteur unitaire

$$\vec{r} = (r_-, r_0, r_+) \quad q = 0, \pm 1$$

$$r_0 = r_z \quad r_{\pm} = \frac{r_x \pm i r_y}{\sqrt{2}}$$



$$\begin{aligned} \vec{r} &\rightarrow \vec{r} \\ r_q &\rightarrow r_q = \left\{ \begin{array}{l} r_0 = z = r \cos \theta \\ r_+ = \frac{x + iy}{\sqrt{2}} = \frac{r}{\sqrt{2}} \sin \theta e^{i\phi} \\ r_- = \frac{y - ix}{\sqrt{2}} = \frac{r}{\sqrt{2}} \sin \theta e^{-i\phi} \end{array} \right. \end{aligned}$$

$$x = r \cos \theta \sin \theta$$

$$y = r \sin \theta \sin \theta$$

$$\langle j_z; j^{w_j} | 1 j^{u_j} \rangle \otimes (1g)$$

$$\rightarrow y_{1,0} = \sqrt{\frac{3}{4\pi}} \cos \theta$$

$$\rightarrow y_{1,\pm 1} = \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi}$$

$$r_q = \sqrt{\frac{4\pi}{3}} \circledcirc y_{1,q} (\theta, \phi)$$

$$\vec{e} \cdot \vec{d} = -e \sum_{q=0, \pm 1} \epsilon_q \circledcirc r_q$$

$$\langle n'l's; j'w_j' | r_q | nls; ju_j \rangle$$

$$= \underbrace{\langle n'l's j' || r || nls j \rangle}_{\sim} \times \underbrace{\langle w_j q; j^{u_j} |}_{j_z}$$

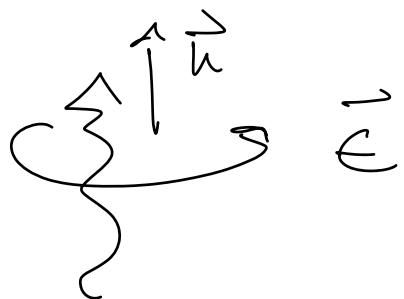
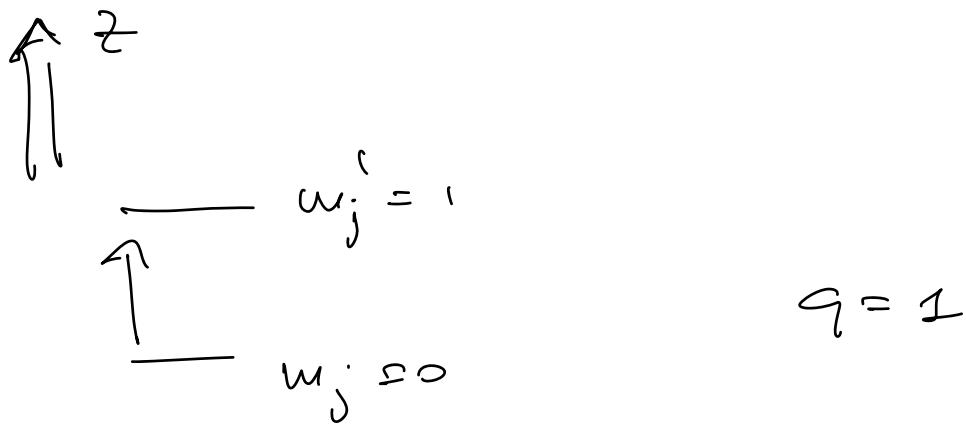
$$\begin{array}{c}
 \hat{\Gamma} \\
 l_1, l_2 \\
 j, 1 \rightarrow j' = |j-1, j, j+1| \\
 \hline
 j' - j = 0, \pm 1
 \end{array}$$

$\Delta n = \text{quelconque}$

$$m_j + q = m'_j$$

$$\underline{\Delta m_j = q}$$

$$\vec{E} = \epsilon_q \vec{u}_q$$



$$|nlS; j^{w_j}\rangle = \sum_{m_{ls}} C_{m_{ls}; j^{w_j}}^{ls} |nlm\rangle \otimes |S_{ms}\rangle$$

$$\begin{aligned} & \langle n'l's; j^{w_j} | (r_q) | nlS; j^{w_j} \rangle \\ &= \sum_{m_{ls}} \sum_{m'_{ls'}} C_{m_{ls}; j^{w_j}}^{ls} C_{m'_{ls'}; j^{w_j'}}^{ls} \\ & \quad \underbrace{\langle nl'm' | (r_q) | nlm \rangle}_{\text{L}} \underbrace{\langle S_{ms'} | S_{ms} \rangle}_{\delta_{m_s, m'_s}} \end{aligned}$$

$$\Rightarrow \langle \gamma; \underline{\ell'_{\text{in}}} | r_g | \langle \gamma; \underline{\ell'_{\text{in}}}) \rangle \neq$$

↑ ↑ ↓
 ↑ ↓ j_{\text{in}}

$$= \langle \gamma; \underline{\ell'} || r || \gamma \ell \rangle$$

↑ ↑ ↑

$$\ell' = |\ell - 1, \ell, \ell + 1$$

$$\Delta \ell = \ell' - \ell = 0, \pm 1$$

$$r_g = \sqrt{\frac{4\pi}{3}} \circledR y_{1g}(\theta, \phi)$$

$$\langle \underline{\ell'_{\text{in}}} | r_g | \underline{\ell'_{\text{in}}} \rangle \neq 0$$

$$= \int d\tau r^2 r R_{nl}(r) R_{nl'}(r)$$

$$\int d\theta d\phi \sin \theta [y_{\ell'_{\text{in}}}(\theta, \phi) y_{1g}(\theta, \phi) y_{\ell'_{\text{in}}}(\theta, \phi)]$$

↑

$$Y_{lm}(\theta, \phi) \rightarrow$$

inversion

$\phi \rightarrow \bar{\phi} + \pi$

$\theta \rightarrow \bar{\theta} + \pi$

$(-1)^l Y_{lm}(\theta, \phi)$

↓

partie sous inversion
seulement

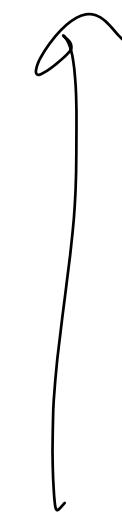
$$(-1)^{l'+l+1} = 1$$

$$\underbrace{l'+l}_{\text{pair}} + 1 = \text{pair}$$

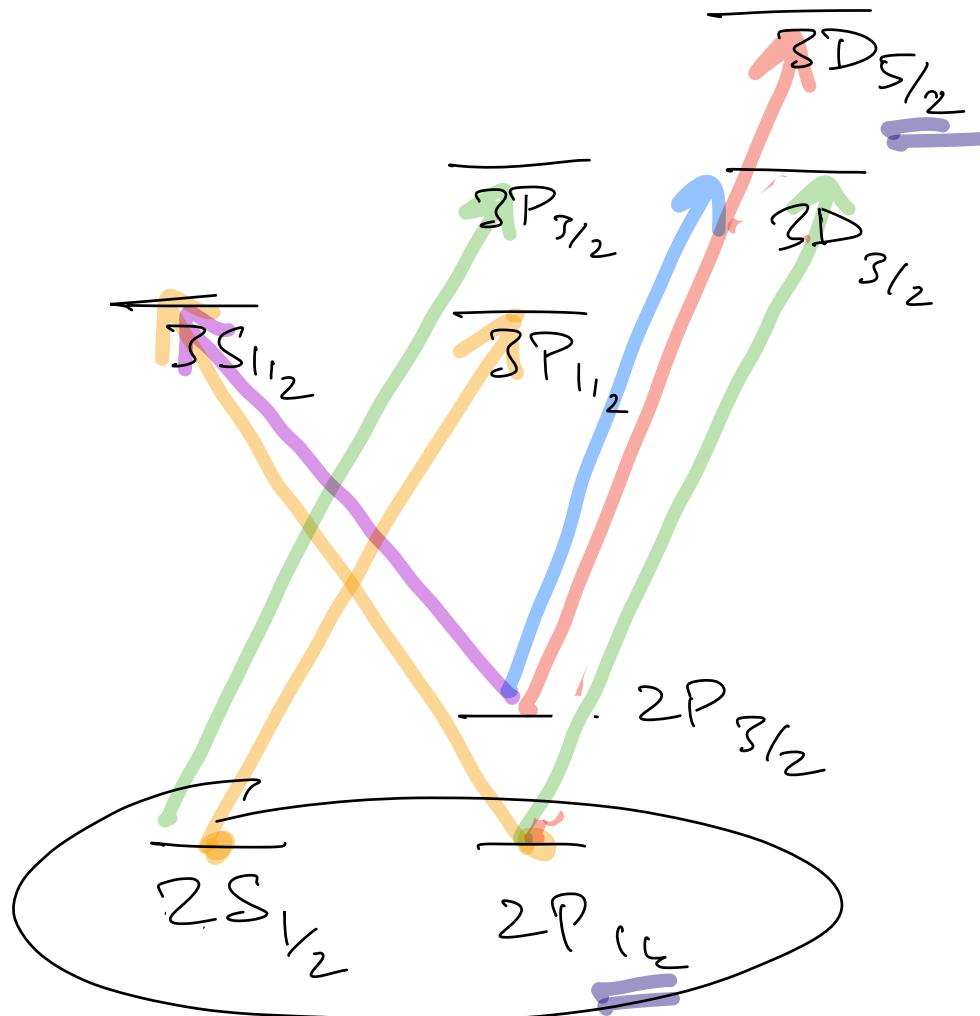
$$\Delta l = l' - l = \cancel{(0)} \pm 1$$

$$\left\{ \begin{array}{l} \Delta n = n' - n = \text{quelque chose ?} \\ \Delta j = j' - j = 0, \pm 1 \\ \Delta l = l' - l = \pm 1 \\ \Delta m_j = m_j' - m_j = q \\ E = \hbar \omega \end{array} \right.$$

$n=3$



$n=2$



$\ell =$

0

1

2

$n=1$

$1S_{1/2}$

Decalage de Lamb ↗

splitting entre

nP_j , nS_j

nP_j , nD_j

