PH 585
AMO

Lecture #5

①

Selection rules

Recall: $\overline{W}_{ab} = \overline{W}_{ba} \sim |M_{ba}|^2$

transition rates

M_{ba}: $\langle \Psi_b | e^{i\vec{k}\cdot\vec{r}}\, \hat{\vec{\varepsilon}}\cdot\vec{D} | \Psi_a \rangle$

If $M_{ba} = 0 \Rightarrow$ transition is <u>strictly</u> forbidden

$$e^{i\vec{k}\cdot\vec{r}} \simeq \underset{\substack{\uparrow\\ \text{electric dipole}\\ \text{approxim.}}}{1} + \underbrace{i\vec{k}\cdot\vec{r}}_{\substack{\text{magnetic dipole}\\ \text{and electric}\\ \text{quadrupole}}} + \ldots$$

If $|M^{D}_{ba}| = 0 \Rightarrow$ transition is forbidden in the electric dipole approx. (but can be allowed in magn. dipole or electric quadrupole app.

Consider $M^{D}_{ba} \Rightarrow \overline{W}^{D}_{\substack{ab\\ ba}} \sim |M^{D}_{ba}|^2 \sim |\hat{\vec{\varepsilon}}\cdot\vec{r}_{ba}|^2$

need this for absorption, stimul. emission, and spont. emission

$$\hat{\vec{\varepsilon}}\cdot\vec{r}_{ba} = (\vec{\varepsilon})_x(\vec{r}_{ba})_x + (\vec{\varepsilon})_y(\vec{r}_{ba})_y + (\vec{\varepsilon})_z(\vec{r}_{ba})_z =$$

$$= (\vec{\varepsilon})^*_1(\vec{r}_{ba})_1 + (\vec{\varepsilon})^*_{-1}(\vec{r}_{ba})_{-1} + (\vec{\varepsilon})^*_0(\vec{r}_{ba})_0$$

↑ in spherical basis.

②

$\vec{\mathcal{E}}_1 = -\frac{1}{\sqrt{2}}\left(\vec{\mathcal{E}}_x + i\vec{\mathcal{E}}_y\right)$; $\mathcal{E}_0 = \mathcal{E}_z$, $\mathcal{E}_{-1} = \frac{1}{\sqrt{2}}(\mathcal{E}_x - i\mathcal{E}_y$

$\vec{\mathcal{E}} = (\mathcal{E}_1, \mathcal{E}_{-1}, \mathcal{E}_0)$ instead of $(\mathcal{E}_x, \mathcal{E}_y, \mathcal{E}_z)$ ↑ right

Then, $$\underset{\underset{0,\pm 1}{\uparrow}}{r_{ba\,q}} = \begin{cases} -\frac{1}{\sqrt{2}}(x+iy) = r\sqrt{\frac{4\pi}{3}}\,Y_{11}(\theta,\varphi) \\ z = r\sqrt{\frac{4\pi}{3}}\,Y_{10}(\theta,\varphi) \quad \text{lin} \\ \frac{1}{\sqrt{2}}(x-iy) = r\sqrt{\frac{4\pi}{3}}\,Y_{1,-1}(\theta,\varphi) \end{cases}$$

$$\vec{\mathcal{E}}\cdot\vec{r}_{ba} = \sum_{q=0,\pm1} \mathcal{E}_q^*(\vec{r}_{ba})_q \Rightarrow$$

$$(\vec{r}_{ba})_q = \sqrt{\frac{4\pi}{3}}\underbrace{\int_0^\infty R_{n'l'}(r)\,R_{nl}(r)\,r^3\,dr}_{\text{always non-zero}} \cdot$$

$$\langle \underset{\underset{n'l'm'}{\uparrow}}{\psi_b} | r_q | \underset{\underset{nlm}{\uparrow}}{\psi_a} \rangle$$

$$\cdot \int Y^*_{l',m'}(\theta,\varphi)\,Y_{1,q}(\theta,\varphi)\,Y_{l,m}(\theta,\varphi)\,d\Omega$$

Recall from Phys 652:

Clebsch-Gordan coeff. ↓ (from Tables)

$$Y_{l_1,m_1}\,Y_{l_2,m_2} = \sum_{l'',m''}\sqrt{\frac{(2l_1+1)(2l_2+1)}{4\pi(2l''+1)}}\,\langle l_1,l_2;0,0|l'',0\rangle \cdot$$

$$\cdot\,\underline{\langle l_1,l_2;m_1,m_2|l'',m''\rangle}\,Y^*_{l'',m''}$$

So, $$\underbrace{|\ell_1, m_1'\rangle \otimes |\ell_2, m_2'\rangle}_{\text{uncoupled basis}} \Rightarrow \underbrace{|\ell, m\rangle}_{\text{coupled basis}} \equiv |\ell_1 \ell_2;$$

uncoupled basis: $\vec{L}_1^2, L_{1z}, \vec{L}_2^2, L_{2z}$

coupled basis: $\vec{L}^2, L_z, \vec{L}_1^2, \vec{L}_2^2$

$$|\ell, m\rangle = \sum_{m_1, m_2} |\ell_1, \ell_2, m_1, m_2\rangle \underbrace{\langle \ell_1 \ell_2, m_1, m_2 | \ell, m\rangle}_{\text{Clebsch-Gordan coefficients}}$$

From the addition of angular moments ⇒ $m = m_1 + m_2$

$$|\ell_1 - \ell_2| \le \ell \le \ell_1 + \ell_2$$

→ unless this is true ⇒ C.-G. coeff. are zero

So, $\overset{\ell_1}{Y_{1,q}}\ \overset{\ell_2}{Y_{\ell,m}} \Rightarrow Y_{\ell'', m+q}$, $\quad |\ell - 1| \le \ell'' \le \ell + 1$

$$\Downarrow$$

$$\ell+1,\ \ell,\ \ell-1$$

$$\int Y^*_{\ell', m'}\, Y_{\ell'', m+q}\, d\Omega \neq 0$$

if $m' = m + q$, $\ell' = \ell''$ → $\ell+1, \ell, \ell-1$

Additional restriction: parity

$$\vec{r} \to -\vec{r} \Rightarrow \begin{matrix} r \to r \\ \theta \to \pi - \theta \\ \varphi \to \varphi + \pi \end{matrix} \Rightarrow \psi_{n\ell m}(\vec{r}) \overset{?}{\Rightarrow} \psi_{n\ell m}(-\vec{r})$$

$$R_{nl}(r)\, Y_{lm}(\theta,\varphi) \rightarrow R_{nl}(r)\, \underbrace{Y_{lm}(\pi-\theta,\varphi+\pi)}$$

$$\|$$

$$\int \underbrace{Y^{*}_{l'm'}}_{\Uparrow} \underbrace{Y_{l'',m+q}}_{\Uparrow} d\Omega = \delta_{l'l''}\,\delta_{m',m+q} \qquad (-1)^{l}\, Y_{lm}(\theta,\varphi)$$

parity: $(-1)^{l'}$ $(-1)^{l''}$ $\Rightarrow (-1)^{l'+l''} \leftarrow$ if odd $\Rightarrow$ integral is zero

but since $l'+l''=2l' \rightarrow$ always even

But: if $Y_{l_1,m_1'}\, Y_{l_2,m_2'} \Rightarrow \underbrace{Y_{l'',m''}}$

$(-1)^{l''+l\pm1}$

$$\underbrace{\overset{\uparrow}{(-1)^{l_1}} \quad \overset{\uparrow}{(-1)^{l_2}}}_{(-1)^{l_1+l_2}} \qquad \overset{\uparrow}{(-1)^{l''}}$$

$(-1)^{l_1+l_2} \leftrightarrow$ parity should match

So, if $l_1=1$, $l_2=l \Rightarrow (-1)^{l+1}$ should match $(-1)^{l''}$

So, $l''=l\pm1$ (but not $l''=l$)

So, selection rules for an electric dipole approximation: $\underbrace{\Delta l}_{l'-l} = \pm 1$, $\underbrace{\Delta M}_{m'-m} = q \leftarrow 0, \pm 1$

linear $\parallel Oz$; circular

depends on polarisation!

$l'+l+1$

$l'+l''=$

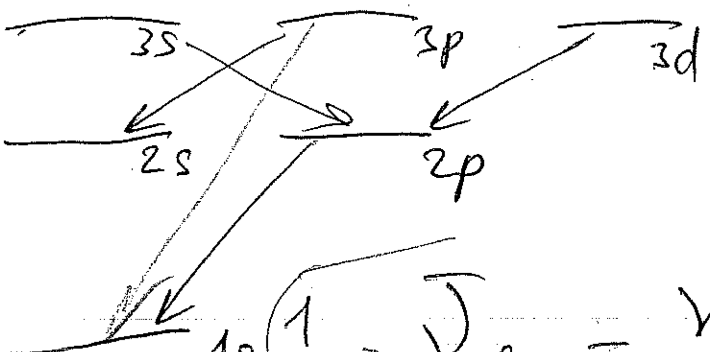
Note: for magnetic dipole / electric quadrupole ⇒ have

$$\int Y_{l'm'} \, Y_{2q} \, Y_{lm} \, d\Omega \qquad \sim |r^2_{ba}|$$

⇓

selection rules are $\Delta l = 0, \pm 2$

Ex. Transitions for Ⓗ-atom



"Bare bones" Ⓗ (only Coulomb interaction is taken into account)

⇓

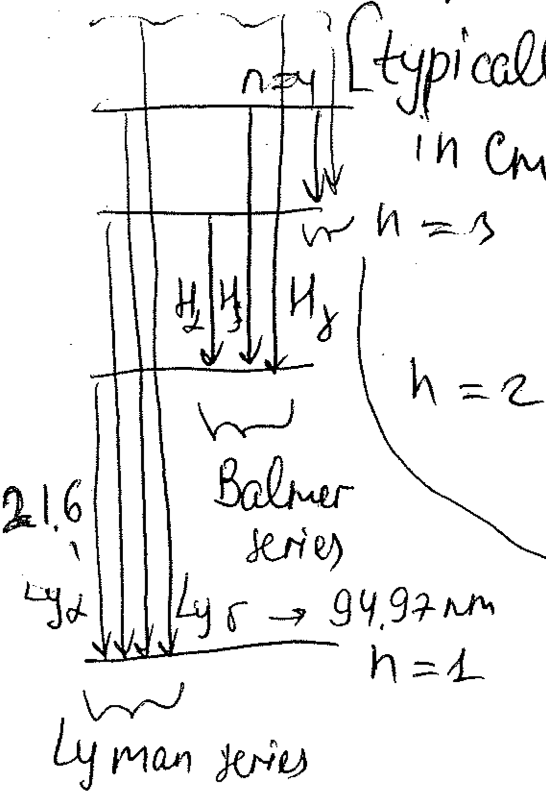
$$\boxed{\frac{1}{\lambda} = \bar{\nu}_{ab}} = \frac{\nu_{ab}}{c} = Z^2 \boxed{E_I^{(H)}/hc} \left[\frac{1}{n_a^2} - \frac{1}{n_b^2}\right]$$

↑ wave number [typically in cm-1]

↑ freq. of transition

also known as $R = 109737 \text{ cm}^{-1}$

↑ Rydberg constant



H_α : 656.3 nm

H_β : 486.1 nm → identified in star atmosphere (Fraunhofer (1817))

H_γ : 434 nm

Paschen series ⇒ 1.875 μm, 1.2818 μm

↗ Pa

Then, Brackett series etc

Br ↗

Note: 1) Electric field dipole operator doesn't couple spin states

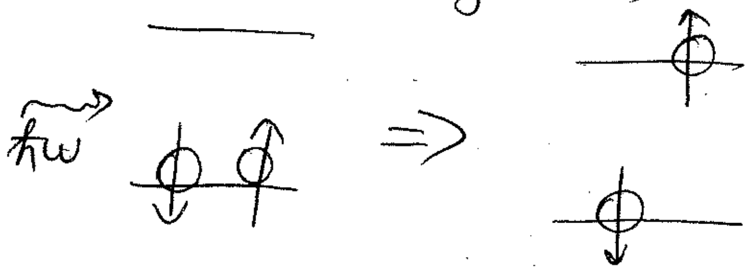
If $\Psi_a \Leftrightarrow |n\, l\, m\rangle_a \otimes |s, m_s\rangle_a$

$\Psi_b \Leftrightarrow |n\, l\, m\rangle_b \otimes |s, m_s\rangle_b$

$$\langle \Psi_a | \vec{\mathcal{E}} \cdot \vec{r}_{ab} | \Psi_b \rangle = {}_a\langle n l m | \vec{\mathcal{E}} \cdot \vec{r}_{ab} | n l m \rangle_b \cdot$$

$$\cdot \underbrace{{}_a\langle s, m_s | s, m_s \rangle_b}_{\delta_{m_{sa}, m_{sb}}}$$

$\Rightarrow$ i.e. spin state is unchanged $\Rightarrow$



2) If $\Delta l = \pm 1$ as a result of transition $\Rightarrow$ change in angular momentum of the atom $\Rightarrow$ where does it go? (conservation laws!) $\Rightarrow$ photon!

$$\vec{J} = \frac{1}{c^2}\int_V \vec{r} \times \vec{S}\, dV$$

$\uparrow$ angular momentum of EM field in a volume V

$\vec{S}$: $\uparrow$ $\frac{c}{4\pi}\vec{E}\times\vec{H} \leftarrow$ Poynting

linear polarization is a combination of these $\longrightarrow$ right- and left-hand polarization

$\downarrow$ $\boxed{\pm}\,\hbar$ angular mom.'s

On a particle level: photon $\Rightarrow$ spin $s = 1$, helicity ± 1 $\nearrow$