Selection Rule: Need to evaluate $\hat{E} \cdot \vec{r}_{ba}$

$\downarrow$

$\langle \phi_b | \vec{r} | \phi_a \rangle$

Atomic wavefunctions:

$\phi(\vec{r}) = \phi(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi)$;

It is therefore convinient to express $\hat{E}$ and $\vec{r}$ in terms of sph^{c} harmonics

Result: $Y_{00} = \frac{1}{\sqrt{4\pi}}$; $Y_{10} = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$; $Y_{1,\pm 1} = \mp\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta \, e^{\pm i\phi}$

$\Rightarrow z = r\cos\theta = r\left(\frac{4\pi}{3}\right)^{1/2} Y_{10}$

$x = r\sin\theta\cos\phi = \frac{1}{2} r\sin\theta \left[e^{i\phi} + e^{-i\phi}\right]$

$= \frac{r}{2}\left(\frac{8\pi}{3}\right)^{1/2}\left[Y_{1,-1} - Y_{1,1}\right]$

$y = r\sin\theta\sin\phi = \frac{ir}{2}\left(\frac{8\pi}{3}\right)^{1/2}\left[Y_{1,1} + Y_{1,-1}\right]$

Let $\phi_a = R_{nl}(r) Y_{lm}(\theta, \phi)$

$\phi_b = R_{n'l'}(r) Y_{l'm'}(\theta, \phi)$

$\therefore$ If $\underline{\underline{\hat{E} \parallel \hat{z}}}$: $\hat{E} \cdot \vec{r}_{ba} = z_{ba} = \left(\frac{4\pi}{3}\right)^{1/2} \underbrace{\int R^*_{n'l'} \, r R_{nl} \, dr}_{r_{n'l'nl}} \underbrace{\int Y^*_{l'm'} Y_{10} Y_{lm} \, d\theta \, d\phi}_{\Omega^{1,0}_{l'm'lm}}$

Similarly if $\hat{E} \perp \hat{z}$:

$\hat{E} \cdot \vec{r}_{ba} = \frac{E_x}{|E|} x_{ba} + \frac{E_y}{|E|} y_{ba}$

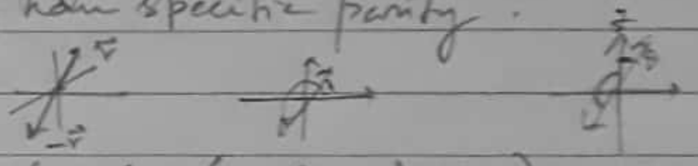
$= \frac{E_x}{|E|}\left(\frac{2\pi}{3}\right)^{1/2} r_{n'l'nl}\left[\Omega^{1,-1}_{l'm'lm} - \Omega^{1,1}_{l'm'lm}\right] + \frac{iE_y}{|E|}\left(\frac{2\pi}{3}\right)^{1/2} r_{n'l'nl}\left[\Omega^{1,1}_{l'm'lm} + \Omega^{1,-1}_{l'm'lm}\right]$

Note that $r_{n'l'nl}$ is always non zero (sph. symm)

$\therefore$ Transition can be forbidden only if $\Omega^{1q}_{l'm'lm}$ is zero.

Y_{lm} are not all sph symm but they have specific parity.

Parity : $\vec{r} \to -\vec{r}$ inversion



$$R_{nl}(r) Y_{lm}(\theta,\phi) \to R_{nl}(r) Y_{lm}(\pi-\theta, \phi+\pi)$$

$$= R_{nl}(r) (-1)^{l} Y_{lm}(\theta,\phi)$$

$$\therefore \vec{r} \to -\vec{r} \Rightarrow \Omega^{1q}_{l'm'lm} \to (-1)^{l'+l+1} \Omega^{1q}_{l'm'lm}$$

$\therefore \Omega^{1q}_{l'm'lm} \neq 0$ If. $l'+l+1 =$ even

$\Rightarrow \underline{l'+l = \text{odd}}$

Recall, $Y_{lm}(\theta,\phi) = P_l^m(\cos\theta)\, e^{im\phi}$

$\hookrightarrow$ Associated Legendre fn. (Recall: Legendre Polynomial $P_l(\cos\theta)$)

$\therefore$ The Azimuthal (ϕ) part of Ω : $\int_0^{2\pi} e^{i(m+q-m')\phi} d\phi$

$\neq 0$ if $m+q-m'=0$

$\therefore$ If $\hat{E} \parallel \hat{z}$: $q=0 \Rightarrow \underline{\Delta m = 0}$

If $\hat{E} \perp \hat{z}$; $q = \pm 1 \Rightarrow \underline{\Delta m = \pm 1}$

} Selection rule on magnetic quantum #

The orbital part (θ) of Ω : $\int_{-\pi}^{\pi} P^{m'}_{l'} P^{q}_{1} P^{m}_{l} \sin\theta\, d\theta$

$\hat{E} \parallel \hat{z}$; $q=0 \Rightarrow \int_{-1}^{1} P_l^m \, P_{l'}^m \, P_1^0 \, d(\cos\theta)$ $\quad \because \Delta m = 0$

$\hat{E} \perp \hat{z}$; $q=\pm 1 \Rightarrow \int P_l^m \, P_{l'}^{m\pm 1} \, P_1^{\pm 1} \, d(\cos\theta)$ $\quad \because \Delta m = \pm 1$

Properties of Associated Legendre polynomial

(a) $\rightarrow$ $$(2l+1)\cos\theta \, P_l^m = (l+1-m)\, P_{l+1}^m + (l+m)\, P_{l-1}^m$$

(b) $\rightarrow$ $$(2l+1)\sin\theta \, P_l^m = P_{l+1}^{m+1} - P_{l-1}^{m+1}$$

(c) $\rightarrow$ normalization: $$\int_{-1}^{1} P_l^m \, P_{l'}^m \, d(\cos\theta) = \left(\frac{2}{2l+1}\right)\frac{(l+m)!}{(l-m)!}\,\delta_{ll'}$$

If $\hat{E} \parallel \hat{z}$: $q=0 \Rightarrow$ substitute $(P_l^m \, P_1^0)$, that is $(P_l^m \cos\theta)$ by (a):

$$\int\left[\frac{(l+1-m)}{(2l+1)} P_{l+1}^m \, P_{l'}^m + \left(\frac{l+m}{2l+1}\right) P_{l-1}^m \, P_{l'}^m\right] d(\cos\theta)$$

$\neq 0$ only if $l' = l \pm 1$ by (c)

$\therefore$ If $\hat{E} \perp \hat{z}$: $q = +1$; substitute $(P_l^m \, P_1^1)$ or $(P_l^m(-\sin\theta))$ by (b)

$$-\int\left[\frac{1}{(2l+1)} P_{l+1}^{m+1} \, P_{l'}^{m+1} - \frac{1}{(2l+1)} P_{l-1}^{m+1} \, P_{l'}^{m+1}\right] d(\cos\theta)$$

Similarly if $q = -1$: $$\frac{1}{2}\int\left[\frac{1}{(2l+1)} P_{l+1}^{m+1} \, P_{l'}^{m+1} - \frac{1}{(2l+1)} P_{l-1}^{m+1} \, P_{l'}^{m+1}\right] d(\cos\theta)$$

$P_1^{-1} = -\frac{1}{2} P_1^1$

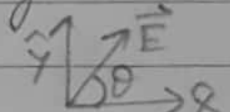
$\therefore$ for $q \pm 1$ the orbital part to be nonzero $l' = l \pm 1$

$\therefore$ If $q=0$: $\Delta m = 0$, $\Delta l \;\pm 1 \longrightarrow \hat{E} \parallel \hat{z}$

$q = \pm 1$: $\Delta m = \pm 1$, $\Delta l = \pm 1 \longrightarrow \hat{E} \perp \hat{z}$

Recall that quantum numbers l and m are associated with angular momentum: $\sqrt{l(l+1)}\,\hbar$ with component $m\hbar$ along direction of azimuthal symmetry ($\hat{z}$).

Therefore selection rule appear to violate conservation of angular momentum. Turns out that the balance angular momentum is carried in or out by the photons. Let us see how. Let $\hat{E} \parallel \hat{z}$

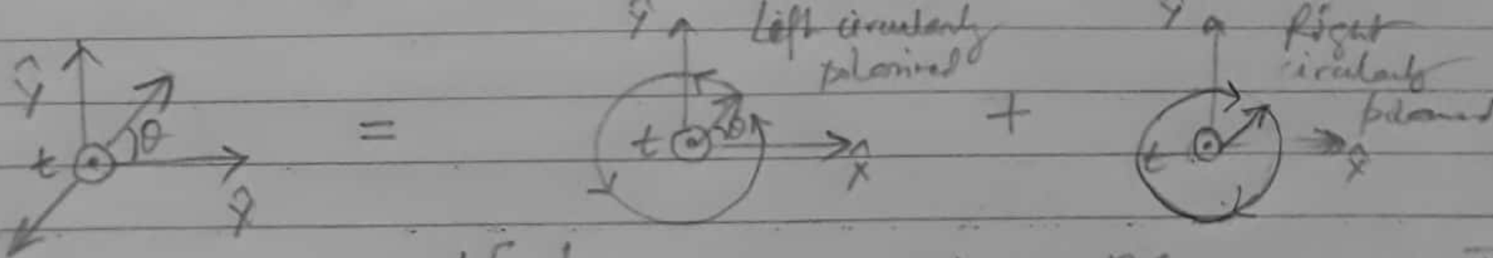


$$\vec{E} = \left(E_0 \cos\theta\,\hat{x} + E_0 \sin\theta\,\hat{y}\right)\cos(\vec{k}\cdot\vec{z} - \omega t + \delta_\omega)$$

$$= E_0\,\hat{x}\cos\theta\cos(kz - \omega t + \delta_\omega) + E_0\,\hat{y}\sin\theta\cos(kz - \omega t + \delta_\omega)$$

$$= E_0\,\hat{x}\left[\frac{\cos(\theta + kz - \omega t + \delta_\omega) + \cos(\theta - kz + \omega t - \delta_\omega)}{2}\right] + E_0\,\hat{y}\left[\frac{\sin(\theta + kz - \omega t + \delta_\omega) + \sin(\theta - kz + \omega t - \delta_\omega)}{2}\right]$$

$$= \frac{E_0}{2}\left[\hat{x}\cos(kz - \omega t + \delta_\omega + \theta) + \hat{y}\sin(kz - \omega t + \delta_\omega + \theta)\right] + \frac{E_0}{2}\left[\hat{x}\cos(kz - \omega t + \delta_\omega - \theta) - \hat{y}\sin(kz - \omega t + \delta_\omega - \theta)\right]$$



$$= \frac{1}{2}\left[E^L(kz - \omega t + \delta_\omega + \theta) + E^R(kz - \omega t + \delta_\omega - \theta)\right]$$

Note: $E^L(\dots) = E_0\,\hat{x}\left[\frac{e^{i(\dots)} + e^{-i(\dots)}}{2}\right] + E_0\,\hat{y}\left[\frac{e^{i(\dots)} - e^{-i(\dots)}}{2i}\right]$

$$= E_0\,\hat{x}\left[\frac{e^{i(\dots)} + e^{-i(\dots)}}{2}\right] - iE_0\,\hat{y}\left[\frac{e^{i(\dots)} - e^{-i(\dots)}}{2}\right]$$

$$= E_0 \left[\frac{e^{i(\cdots)}}{2} (\hat{x} - i\hat{y}) + \frac{e^{-i(\cdots)}}{2} (\hat{x} + i\hat{y}) \right]$$

$$= \frac{E_0}{\sqrt{2}} \left[e^{i(\cdots)} \hat{e}' + cc \right] \; ; \; \hat{e}' = \frac{1}{\sqrt{2}}(\hat{x} - i\hat{y})$$

Similarly $E^R(\cdots) = \frac{E_0}{\sqrt{2}} \left[e^{i(\cdots)} \hat{e}'' + cc \right] \; ; \; \hat{e}'' = \frac{1}{\sqrt{2}}(\hat{x} + i\hat{y})$, $\hat{e}'' = \hat{e}'^{*}$

* Now recall:

$$C_b^D(t) = \frac{-e}{2m} \int d\omega A_0(\omega) \left[e^{i\delta_\omega} \left(M^D_{ba} = \frac{m(-\omega_{ba})}{\hbar} \hat{E} \cdot \vec{r}_{ba} \right) \underbrace{\left[\frac{e^{i(\omega_{ba} - \omega)t'}}{(\omega_{ba} - \omega)} \right]^t}_{\text{Absorption}} + e^{-i\delta_\omega} M^D_{ba} \underbrace{\left[\frac{e^{i(\omega_{ba} + \omega)t'}}{(\omega_{ba} + \omega)} \right]^t_0}_{\text{Emission}} \right]$$

$$* \; \vec{E} = \frac{1}{2} \left[E^L(kz - \omega t + \delta_\omega + \theta) + E^R(kz - \omega t + \delta_\omega - \theta) \right]$$

$$= \frac{1}{2} \times \frac{E_0}{\sqrt{2}} \times \left[e^{i(\cdots + \theta)} \hat{e}' + e^{-i(\cdots + \theta)} \hat{e}'' + e^{i(\cdots - \theta)} \hat{e}'' + e^{-i(\cdots - \theta)} \hat{e}' \right]$$

Since $E = -\frac{\partial A}{\partial t}$ the above $\vec{E}$ suggests that the $\langle | \vec{A} \cdot \nabla | \rangle$ term in $C_b(t)$ after dipole approximation would lead to terms involving:

E^L

(1) $e^{i(\delta_\omega - \omega t + \theta)} \hat{e}' \cdot \vec{r}_{ba}$ $\longrightarrow$ absorption (see $C_b^D(t)$)

(2) $e^{-i(\delta_\omega - \omega t + \theta)} \hat{e}'' \cdot \vec{r}_{ba}$ $\longrightarrow$ emission

$\left\{ \begin{array}{l} -\omega t \to \text{Absorption} \\ +\omega t \to \text{Emission} \end{array} \right.$

E^R

(3) $e^{i(\delta_\omega - \omega t - \theta)} \hat{e}'' \cdot \vec{r}_{ba}$ $\longrightarrow$ absorption

(4) $e^{-i(\delta_\omega - \omega t - \theta)} \hat{e}' \cdot \vec{r}_{ba}$ $\longrightarrow$ emission

①,④ : $\hat{e}^{L}\cdot\vec{r}_{ba} = \frac{1}{\sqrt{2}}\left(x_{ba} - i\,y_{ba}\right) = \# \langle |Y_{1,1}| \rangle$

②,③ : $\hat{e}^{R}\cdot\vec{r}_{ba} = \frac{1}{\sqrt{2}}\left(x_{ba} + i\,y_{ba}\right) = \# \langle |Y_{1,-1}| \rangle$

$\therefore$ for ① and ④ selection rule is $\Delta m = +1$
for ② and ③ " " " $\Delta m = -1$

$\therefore$ ① E^L left circularly polarized $\Rightarrow \Delta m = +1 \Leftarrow$ ④ E^R Right circularly pol.

② E^R right circ. pol. $\Rightarrow \Delta m = -1 \Leftarrow$ ③ E^L left circ. pol.

$\therefore$ Conservation of total angular momentum of field and particle
$\Rightarrow$ left circularly pol light has "spin" or "helicity" +1 leads to component of angular momentum along direction of propagation. $+\hbar$

Similarly right circularly pol. light carries angular momentum component $-\hbar$ along the direction of propagation of light

The selection rule $\Delta l = \pm 1$ implies the light has odd parity.

Now let us go one term beyond dipole transition!

Recall, $M_{ba} = \langle \phi_b | e^{i\vec{k}\cdot\vec{r}} \hat{E}\cdot\nabla | \phi_a \rangle$

let us retain $i\vec{k}\cdot\vec{r}$ of $\exp(i\vec{k}\cdot\vec{r})$

$$M_{ba} = \int \Psi_b^* \underbrace{(1}_{\text{Dipole transitn}} + \underbrace{i\vec{k}\cdot\vec{r}}_{\bar{M}_{ba}}) \hat{E}\cdot\nabla\Psi_a \, dr$$

$$\bar{M}_{ba} = \int \Psi_b^* \, i\vec{k}\cdot r \, \hat{E}\cdot(\nabla\phi_a) \, dr$$

let $\hat{k} \parallel \hat{z}$, $\hat{E} \parallel \hat{x}$: $\bar{M}_{ba} = \frac{\omega}{c}\int \Psi_b^* \, i z \frac{\partial\Psi_a}{\partial x} \, dr$; $k = \frac{\omega}{c}$

$$= \frac{\omega}{c}\int \Psi_b^* \, iz \, (-i\hbar)^{-1} \hat{p}_x \Psi_a \, dr$$

$$= -\frac{1}{\hbar}\frac{\omega}{c}\int \Psi_b^* \, z \hat{p}_x \Psi_a \, dr = \frac{\overset{\omega_{ba}}{\omega}}{\hbar c}\langle b | z\hat{p}_x | a \rangle$$

$$\boxed{\text{Recall } \hat{p}_x = m(i\hbar)^{-1}[\hat{x}, \hat{H}_0]} = \frac{-\omega}{c}\langle b | z\hat{p}_x | a \rangle = \frac{-\omega}{c} m (i\hbar)^{-1} \langle b | z [x, H_0] | a \rangle$$

$$= -\frac{\omega m}{c}(i\hbar)^{-1}\langle b | z x H_0 - \underbrace{z H_0 x}_{\text{problem?}} | a \rangle$$

Turns out that:

$$\langle b | p_z x | a \rangle = m(i\hbar)^{-1}\langle b | [z H_0] x | a \rangle = m(i\hbar)^{-1}\langle b | \underline{z H_0} x - H_0 z x | a \rangle$$

$$\langle b | p_z x | a \rangle + \langle b | z p_x | a \rangle = \langle b | xz | a \rangle (E_b - E_a)$$

Note: $L_y = z p_x - p_z x \Rightarrow \underline{\langle b | z p_x | a \rangle} - \langle b | L_y | a \rangle + \underline{\langle b | z p_x | a \rangle} = \langle b | xz | a \rangle \times m\hbar\omega_{ba} \times (i\hbar)^{-1}$

$$\therefore \bar{M}_{ba} = \frac{-\omega_{ba}}{\hbar c}\langle b | z p_x | a \rangle = \underbrace{-\frac{\omega_{ba}}{2\hbar c}\langle b | L_y | a \rangle}_{\text{term due to orbital magnetic moment}} - \underbrace{i\frac{m\omega_{ba}^2}{2\hbar c}\langle b | xz | a \rangle}_{\text{Electric Quadrupole moment term}}$$

$L = r \times p$

$$\begin{vmatrix} i & j & k \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

$i(y p_z - p_y z) = L_x$

$j(z p_x - p_z x) = L_y$

$z(x p_y - p_x y) = L_z$

magnetic dipole transition

Electric Quadrupole transition

$$\bar{M}_{ba} = \cancel{*} - \frac{\omega_{ba}}{2\hbar c}\langle b|L_y|a\rangle - i\frac{m\,\omega_{ba}^2}{2\hbar c}\langle b|xz|a\rangle$$

$[L^2, L_y] = 0$ $\Delta l = 0$

$\Delta l = 0, \pm 2$

Dipole term is there (Do not forget)

Recall the derivation of $\Delta l = \pm 1$

The above integrand is of form $\int P_l^m P_{l'}^{m/m\pm1}$ $P^0_1(\# P^1_1 + \# P^{-1}_1)$ some numbers.

$= \int P_l^m P_{l'}^{m/m\pm1} \cos\theta \sin\theta \, d\theta$

$\left(\left(P_l^m \cos\theta\right)\sin\theta\right)$

$\Delta l = \pm 1$

$\Delta l = \pm 1 \pm 1 = 0, \pm 2$

Azimuthal part:

$$\Rightarrow \int_0^{2\pi} e^{i(m + q_1 + q_2 - m')\phi}\, d\phi$$

(q_1: x, q_2: z)

$\Delta m = \pm 1$; $\Delta m = 0$

It can be $\langle b|xy|a\rangle$ as well. (± 1, ± 1)

$\therefore$ In general!

$$\boxed{\begin{aligned}\Delta l &= 0, \pm 2 \\ \Delta m &= 0, \pm 1, \pm 2\end{aligned}}$$

beyond dipole transition.

Note! $\Delta l = \pm 2$ is pure Quadrupole transition

since the magnetic dipole transition selection rule is $\Delta l = 0$.