$$Y_{10} Y_{\ell m} = \alpha_z Y_{\ell+1,m} + \beta_z Y_{\ell-1,m}$$

$$\int Y^*_{\ell' m'} Y_{10} Y_{\ell m} \, d\Omega = \alpha_z \int Y^*_{\ell', m'} Y_{\ell+1, m} \, d\Omega + \beta_z \int Y^*_{\ell', m'} Y_{\ell-1, m} \, d\Omega$$

$\ell' = \ell \pm 1 \quad m' = m \quad \Rightarrow \Delta m = 0, \; \Delta \ell = \pm 1$

For ξ, η $\quad \int Y^*_{\ell', m'} Y_{1, \pm 1} Y_{\ell, m} \, d\Omega$

$\Delta \ell = \pm 1, \; \Delta m = \pm 1$

The general selection rules for dipole transition

$\Delta \ell = \pm 1 \quad \Delta m = 0, \pm 1$

for z (along z axis) $\Delta \ell = \pm 1, \Delta m = 0$

Example 2

$$\Psi_{nlms} = R_{nl} \cdot Y_{lm} \cdot \sigma_S$$

$$\int \Psi^*_{nlms} \Psi_{n'l'm's'} \, dV = \delta_{nn'} \delta_{ll'} \delta_{mm'} \delta_{ss'}$$

$$\frac{dP_{mn}}{dt} = \frac{\pi e^2 E_0^2}{\hbar^2} |z_{mn}|^2 \quad |x_{mn}|^2 \quad |y_{mn}|^2 \qquad x_{ij} = \int \Psi^*_{n'l'm'} \, x \, \Psi_{nlm} \, dV$$

$\Psi_{nlm} = R_{nl}(r) Y_{lm}(\theta, \varphi)$ for spherical coordinates

$$\underbrace{x = r \sin\theta \cos\varphi \quad y = r \sin\theta \sin\varphi \quad z = r\cos\theta}$$

to simplify calculation we use the linear combination of x and y

$$\xi = x + iy = r \sin\theta \, e^{i\varphi} \qquad z = r \cdot \cos\theta$$

$$\eta = x - iy = r \sin\theta \, e^{-i\varphi}$$

$$Y_{1,1} = -\sqrt{\frac{3}{8\pi}} \sin\theta \cdot e^{i\varphi} \qquad Y_{1,-1} = \sqrt{\frac{3}{8\pi}} \sin\theta \cdot e^{-i\varphi} \qquad Y_{1,0} = \sqrt{\frac{3}{4\pi}} \cos\theta$$

$$\xi = -\sqrt{\frac{8\pi}{3}} \cdot r \cdot Y_{1,1} \qquad \eta = \sqrt{\frac{8\pi}{3}} \cdot r \cdot Y_{1,-1} \qquad z = \sqrt{\frac{4\pi}{3}} \cdot r \cdot Y_{1,0}$$

(z)

solid angle

$$z_{ij} = \int \Psi^*_{nlm} \, z \, \Psi_{n'l'm'} \, dV = \left\{ \int_0^\infty R_{n'l'} R_{nl} r^3 \, dr \cdot \int Y_{l'm'} Y_{1,0} Y_{lm} \, d\Omega \right\} \sqrt{\frac{4\pi}{3}}$$

$$\int Y_{l'm'} Y_{1,0} Y_{l,m} \, d\Omega = ?$$

Transition probability per tim unit:

$$\frac{dP^A_{mn}}{dt} = \frac{2\pi}{\hbar} |h_{mn}|^2 \delta(E_m - E_n - \hbar\omega)$$

for radiation process:

$$\frac{dP^R_{mn}}{dt} = \frac{2\pi}{\hbar} |h_{mn}|^2 \delta(E_m - E_n + \hbar\omega)$$

at follow-up we assume that energy was chosen correctly

External electromagnetic field:

$$\vec{E} = \vec{E}_0 \cos(\omega t - \vec{k}\vec{r}) \qquad k = \frac{2\pi}{\lambda} \qquad \lambda = 5 \cdot 10^{-7} \qquad d \ll \lambda$$

$$d \approx 10^{-10}\, m$$

$$\downarrow$$

$$\vec{E} = \vec{E}_0 \cos(\omega t)$$

$$\vec{E}_0 = (0, 0, E_0) \qquad \hat{H}' = eZE_0 \cos(\omega t) = \frac{eZE_0}{2}(e^{i\omega t} + e^{-i\omega t})$$

$$h = h^*$$

$$\frac{dP^{n \to m}_{nm}}{dt} = \frac{\pi e^2 E_0^2}{\hbar^2} |Z_{mn}|^2 \; ; \quad Z_{mn} = \int \varphi_m^* Z \varphi_n dV ;$$

Example 1 selection rules

what kind of transitions allowed or ... forbidden

n+1

n

n-1

} equidistant

$$\frac{dP_{mn}}{dt} = \frac{\pi e^2 E_0^2}{\hbar^2} |Z_{mn}|^2$$

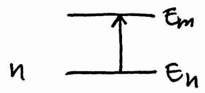
$$Z_{mn} = \int \varphi_m^* z \varphi_n dz \neq 0 \text{ if } m = n \pm 1$$

selection rule

After integration we have:

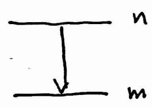
$$C_m^1(t) = -\frac{1}{\hbar}\left\{ h_{mn} \frac{e^{i(\omega_{mn}-\omega)} - 1}{\omega_{mn}-\omega} + h^* \frac{e^{i(\omega_{mn}+\omega)t} - 1}{\omega_{mn}+\omega} \right\}$$

$$\omega_{mn} = \frac{E_m - E_n}{\hbar} \qquad c = \lambda\nu \Rightarrow \nu = \frac{c}{\lambda} \approx \frac{3\cdot 10^{10}}{5\cdot 10^{-7}} \approx 10^{+17}\ Hz$$



① $E_m > E_n$ absorb energy

underside $\omega_{mn}+\omega$ ~~[illegible]~~ tends to $\to \infty$ and second term can be omited.



② $E_m < E_n$

transition from top to bottom level

Energy must be radiated

We start from absorbtion processes:

$$C_m^1 = -\frac{h_{mn}}{\hbar} \cdot \frac{e^{i(\omega_{mn}-\omega)t} - 1}{\omega_{mn}-\omega}$$

$$|C_m^1|^2 = \frac{4|h_{mn}|^2}{\hbar^2} \cdot \frac{\sin^2\left\{\frac{\omega_{mn}-\omega}{2}\cdot t\right\}}{(\omega_{mn}-\omega)^2}$$

$$\delta(x) = \lim_{\lambda\to\infty} \frac{\sin^2(\lambda x)}{\pi\cdot\lambda\cdot x^2} \qquad \delta(x) = \lim_{\lambda\to\infty} \frac{\sin(\lambda x)}{\pi x}$$

$$\lim_{t\to\infty}\left\{\frac{\sin^2\left(\frac{\omega_{mn}-\omega}{2}t\right)}{\pi\left(\frac{\omega_{mn}-\omega}{2}\right)^2}\right\}\frac{\pi t}{4} = \delta\left(\frac{\omega_{mn}-\omega}{2}\right)\cdot\frac{\pi t}{4} = \frac{\pi t}{2}\delta(\omega_{mn}-\omega)$$

$$\underset{n\to m}{P_{nm}} = \frac{2\pi}{\hbar^2}|h_{mn}|^2 \cdot t \cdot \delta(\omega_{mn}-\omega)$$

For zero order approximation

0-order $\frac{\partial C_m^0}{\partial t} = 0$ can be inserted to next equation
auytransitions are impossible

1-order $i\hbar \frac{\partial C_m^1}{\partial t} = \sum_n C_n^0 H' e^{i\omega_{mn} t}$ can be calculated step by step

2-order $i\hbar \frac{\partial C_m^2}{\partial t} = \sum_n C_n^1 H'_{mn} e^{i\omega_{mn} t}$

⋮

if we assume than at the begining system is in state n. It means that

~~C~~ $C_m^0 = \delta_{nm}$

For first order approximation ~~of~~ ~~…~~ we have equation:

$$i\hbar \frac{\partial C_m^1}{\partial t} = e^{i\omega_{mn} t} \cdot H'_{mn}$$

n

$|C_m^1|^2$ - has transition probability value

level $n \to m$

$$C_m^1(t) = \frac{1}{i\hbar} \int_0^t e^{i\omega_{mn}\tau} H'_{mn}(\tau)\, d\tau$$

II Harmonic perturbation

~~This~~ For atom ~~located~~ in external electromagnetic wave. The perturbation operator is:

$$\hat{H}' = \hat{h} \cdot e^{-i\omega t} + \hat{h}^* e^{+i\omega t}$$

$$H'_{mn} = h_{mn} e^{-i\omega t} + h^*_{mn} e^{+i\omega t}$$

$$C_m^1 = \frac{1}{i\hbar} \int_0^t \left\{ h_{mn} e^{i(\omega_{mn}-\omega)\tau} + h^*_{mn} e^{i(\omega_{mn}+\omega)\tau} \right\} d\tau$$

Time dependent perturbation theory

The initial task is:

$$\hat{H}_0 \psi_n = E_n \psi_n$$

Time dependent equation is looks like so:

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}_0 \psi$$

$$\psi(\vec{r},t) = \sum_n C_n e^{-\frac{iE_n t}{\hbar}} \cdot \varphi_n(\vec{r})$$ – time dependent solution

$$\int \psi^* \psi \, dV = 1$$

$$\int \sum_n C_n^* e^{+iE_n t/\hbar} \cdot \varphi_n^* \cdot \sum_{n'} C_{n'} e^{-iE_{n'} t/\hbar} \varphi_{n'} \, dV =$$

$$= \sum_{n,n'} C_n^* C_n e^{i(E_n - E_{n'})t/\hbar} \cdot \int \varphi_n^* \varphi_{n'} \, dV = \sum_n |C_n|^2 = 1$$

The parameters C_n can be interpreted as the probability to find a system in the state with the number n. For stationary task these parameters do not depend on time and the transition between different states are not possible. But what happen for timdependent perturbation. (if we apply)

$$i\hbar \frac{\partial \psi}{\partial t} = (\hat{H}_0 + \hat{H}'(t))\psi$$

and solution:

$$\psi(\vec{r},t) = \sum_n C_n(t) e^{-\frac{iE_n t}{\hbar}} \varphi_n(\vec{r})$$

C_n have ~~and~~ time dependence caused by external perturbation.

$$i\hbar \frac{\partial \psi}{\partial t} = i\hbar \frac{\partial}{\partial t} \sum_n c_n(t) e^{-iE_n t/\hbar} \cdot \varphi_n(\vec{r}) =$$

$$= \sum_n \left\{ i\hbar \cdot \dot{c}_n(t) e^{-iE_n t/\hbar} \cdot \varphi_n + c_n(t) \cdot e^{-iE_n t/\hbar} \cdot E_n \varphi_n \right\} =$$

$$= \sum_n \varphi_n e^{-iE_n t/\hbar} \cdot \left\{ i\hbar \dot{c}_n + c_n E_n \right\}$$

$$(\hat{H}_0 + \hat{H}')\psi = (\hat{H}_0 + \hat{H}') \sum_n c_n e^{-iE_n t/\hbar} \cdot \varphi_n =$$

$$= \sum_n \left\{ \hat{H}_0 c_n \varphi_n + \hat{H}' c_n \varphi_n \right\} e^{-iE_n t/\hbar}$$

$$\times \varphi_m^* \to \int$$

$$\sum_n \int \varphi_m^* \varphi_n \, dv \cdot e^{-iE_n t/\hbar} \left\{ i\hbar \dot{c}_n + c_n E_n \right\} =$$

$$= \sum_n \left\{ c_n \int \varphi_m^* \hat{H}_0 \varphi_n \, dv + c_n \int \varphi_m^* \hat{H}' \varphi_n \, dv \right\} e^{-iE_n t/\hbar}$$

$$\sum_n \delta_{mn} e^{-iE_n t/\hbar} \left\{ i\hbar \dot{c}_n + c_n E_n \right\} = \sum_n \left\{ c_n e^{-iE_n t/\hbar} \left[E_n \delta_{nm} + H'_{nm} \right] \right\}$$

$$e^{-iE_m t/\hbar} \left\{ i\hbar \dot{c}_m + \cancel{c_m E_n} \right\} = \cancel{c_m e^{-iE_m t/\hbar} \cdot E_n} + \sum_n c_n e^{-iE_n t/\hbar} \cdot H'_{nm}$$

$$i\hbar \dot{c}_m = \sum_n c_n e^{i\omega_{mn} t} \cdot H'_{nm}$$

here

$$\omega_{mn} = (E_m - E_n)/\hbar$$

To find the solution of thes equation we use perturabation theory and present c_n as a sequency of differens order approximation (corrections)

$$c_n = c_n^0 + c_n^1 + c_n + \ldots$$

$$i\hbar(\dot{c}_m^0 + \lambda \dot{c}_m^1 + \ldots) = \sum_n (c_n^0 + \lambda c_n^1 + \ldots) e^{i\omega_{mn} t} \cdot \lambda \cdot H'_{nm}$$