LECTURE:4, 5 & 6 (By Anil K Malik)

(Note: All bold symbols are for vector quantities)

TRANSITION RATES FOR ABSORPTION AND EMISSION OF RADIATION

Before interaction:

The joint initial state of atom and radiation is represented as

$$|\phi_i >= |\psi_i > |n_{\lambda,\boldsymbol{k}} >_i \qquad (21)$$

Where $|\psi_i >$ is state of unperturbed atom and $|n_{\lambda,\boldsymbol{k}} >$ is initial state for radiation.

After Interaction:

The joint initial state of atom and radiation is given as

$$|\phi_f >= |\psi_f > |n_{\lambda,\boldsymbol{k}} >_f \qquad (22)$$

Let we consider the case of emission of photon; the final state of radiation will be $|n_{\lambda,\boldsymbol{k}} + 1 >$, then final joint state will be

$$|\phi_f >= |\psi_f > |n_{\lambda,\boldsymbol{k}} + 1 > \qquad (23)$$

Here, electromagnetic field gains the photon.

$$<\phi_f|\hat{v}^+{}_{\lambda,k}|\phi_i > = \frac{e}{m}\sqrt{\frac{2\pi\hbar}{V\omega_k}} < \psi_f|e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\boldsymbol{\varepsilon}^*{}_\lambda \cdot \boldsymbol{P}|\psi_i >< n_{\lambda,\boldsymbol{k}} + 1|\hat{a}^+{}_{\lambda,k}|n_{\lambda,\boldsymbol{k}} >$$

$$= \frac{e}{m}\sqrt{\frac{2\pi\hbar}{V\omega_k}}\sqrt{n_{\lambda,\boldsymbol{k}} + 1} < \psi_f|e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\boldsymbol{\varepsilon}^*{}_\lambda \cdot \boldsymbol{P}|\psi_i > \qquad (24)$$

Where $<n_{\lambda,\boldsymbol{k}} + 1|\hat{a}^+{}_{\lambda,k}|n_{\lambda,\boldsymbol{k}} > = \sqrt{n_{\lambda,\boldsymbol{k}} + 1} < n_{\lambda,\boldsymbol{k}} + 1|n_{\lambda,\boldsymbol{k}} + 1 > = \sqrt{n_{\lambda,\boldsymbol{k}} + 1}$

Similarly, for absorption field loose photon, the final state will be $|\phi_f >= |\psi_f > |n_{\lambda,\boldsymbol{k}} - 1 >$. Hence

$$<\phi_f|\hat{v}_{\lambda,k}|\phi_i > = \frac{e}{m}\sqrt{\frac{2\pi\hbar}{V\omega_k}} < \psi_f|e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\boldsymbol{\varepsilon}_\lambda \cdot \boldsymbol{P}|\psi_i >< n_{\lambda,\boldsymbol{k}} - 1|\hat{a}_{\lambda,k}|n_{\lambda,\boldsymbol{k}} >$$

$$= \frac{e}{m}\sqrt{\frac{2\pi\hbar}{V\omega_k}}\sqrt{n_{\lambda,\boldsymbol{k}}} < \psi_f|e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\boldsymbol{\varepsilon}_\lambda \cdot \boldsymbol{P}|\psi_i > \qquad (25)$$

Where $< n_{\lambda,\boldsymbol{k}} - 1|\hat{a}_{\lambda,k}|n_{\lambda,\boldsymbol{k}} >= \sqrt{n_{\lambda,\boldsymbol{k}}} < n_{\lambda,\boldsymbol{k}} - 1|n_{\lambda,\boldsymbol{k}} - 1 > = \sqrt{n_{\lambda,\boldsymbol{k}}}$

TRANSITION RATES: corresponding to emission or absorption of a photon of energy $\hbar\omega_k = \hbar ck$ are

$$W^{emi} = \frac{4\pi^2 e^2}{m^2 V\omega_k}\left(n_{\lambda,\boldsymbol{k}} + 1\right)\left|< \psi_f|e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\boldsymbol{\varepsilon}^*{}_\lambda \cdot \boldsymbol{P}|\psi_i >\right|^2\delta\left(E_f - E_i + \hbar\omega_k\right) \qquad (26)$$

And

$$W^{abs} = \frac{4\pi^2 e^2}{m^2 V\omega_k}(n_{\lambda,\boldsymbol{k}})\left|< \psi_f\left|e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\boldsymbol{\varepsilon}_\lambda \cdot \boldsymbol{P}\right|\psi_i >\right|^2 \delta\left(E_f - E_i - \hbar\omega_k\right) \quad (27)$$

TRANSITION RATES WITHIN THE DIPOLE APPROXIMATION

Expansion of $e^{\pm i\boldsymbol{k}\cdot\boldsymbol{r}} = 1 \pm i\boldsymbol{k}\cdot\boldsymbol{r} - \frac{1}{2}(i\boldsymbol{k}\cdot\boldsymbol{r})^2 \mp \ldots\ldots\ldots$

For visible or ultraviolet light $kr = \frac{2\pi a_0}{\lambda} \sim 2\pi \times 10^{-10} \sim 0.001$ i.e. very small and incase of γ radiations kr will be even smaller. The electric dipole approximation corresponds to $e^{\pm i\boldsymbol{k}\cdot\boldsymbol{r}} \approx 1$; hence

$$< \psi_f\left|e^{\pm i\boldsymbol{k}\cdot\boldsymbol{r}}\boldsymbol{\varepsilon}_\lambda \cdot \boldsymbol{P}\right|\psi_i > \cong \boldsymbol{\varepsilon}_\lambda \cdot < \psi_f|\boldsymbol{P}|\psi_i > \quad (28)$$

Now $\left[\hat{\boldsymbol{r}}, \hat{H}_0\right] = \frac{i\hbar\hat{\boldsymbol{P}}}{m}$. Hence inserting $\hat{\boldsymbol{P}} = \frac{\boldsymbol{m}}{i\hbar}\left[\hat{\boldsymbol{r}}, \hat{H}_0\right]$ in Eq. (28). Using $\hat{H}_0|\psi_i> = E_i|\psi_i>$ and $\hat{H}_0|\psi_f> = E_f|\psi_f>$, we get

$$\boldsymbol{\varepsilon}_\lambda \cdot < \psi_f|\boldsymbol{P}|\psi_i > = \frac{m}{i\hbar}\boldsymbol{\varepsilon}_\lambda \cdot < \psi_f\left|\left[\hat{\boldsymbol{r}}, \hat{H}_0\right]\right|\psi_i > = \frac{m}{i\hbar}\left(E_i - E_f\right)\boldsymbol{\varepsilon}_\lambda \cdot < \psi_f|\boldsymbol{r}|\psi_i >$$

That gives

$$< \psi_f\left|e^{\pm i\boldsymbol{k}\cdot\boldsymbol{r}}\boldsymbol{\varepsilon}_\lambda \cdot \boldsymbol{P}\right|\psi_i > = \boldsymbol{\varepsilon}_\lambda \cdot < \psi_f|\boldsymbol{P}|\psi_i > = im\omega_{fi}\boldsymbol{\varepsilon}_\lambda \cdot < \psi_f|\boldsymbol{r}|\psi_i > \quad (29)$$

Substituting $< \psi_f\left|e^{\pm i\boldsymbol{k}\cdot\boldsymbol{r}}\boldsymbol{\varepsilon}_\lambda \cdot \boldsymbol{P}\right|\psi_i >$ from Eq. (29) into Eqs. (26) & (27), we get

$$W^{emi} = \frac{4\pi^2 e^2 \omega_{fi}^2}{m^2 V\omega_k}\left(n_{\lambda,\boldsymbol{k}} + 1\right)\left|\boldsymbol{\varepsilon}^*{}_\lambda \cdot < \psi_f|\boldsymbol{r}|\psi_i >\right|^2 \delta\left(E_f - E_i + \hbar\omega_k\right) \quad (30)$$

$$W^{abs} = \frac{4\pi^2 e^2 \omega_{fi}^2}{m^2 V\omega_k}\left(n_{\lambda,\boldsymbol{k}}\right)\left|\boldsymbol{\varepsilon}_\lambda \cdot < \psi_f|\boldsymbol{r}|\psi_i >\right|^2 \delta\left(E_f - E_i - \hbar\omega_k\right) \quad (31)$$

Note:

From Eq. (29), it is clear that transition rate does not vanish even if $n_{\lambda,k} = 0$ (external radiation field) i.e. no perturbation is applied. This shows that spontaneous emission can described along with stimulated emission considering quantization of radiation.

THE ELECTRIC DIPOLE SELECTION RULES

In spherical polar coordinate $\boldsymbol{r} = (rsin\theta cos\varphi)\hat{x} + (rsin\theta sin\varphi)\hat{y} + (rsin\theta)\hat{z}$ and

$$\boldsymbol{\varepsilon}_\lambda \cdot \boldsymbol{r} = r\{(\varepsilon_{x\lambda}sin\theta cos\varphi) + \left(\varepsilon_{y\lambda}sin\theta sin\varphi\right) + (\varepsilon_{z\lambda}sin\theta)\} \quad (32)$$

Using $sin\theta cos\varphi = -\sqrt{\frac{2\pi}{3}}\,(Y_{11} - Y_{1-1})$ and $sin\theta sin\varphi = i\sqrt{\frac{2\pi}{3}}\,(Y_{11} + Y_{1-1})$ and $cos\theta = \sqrt{\frac{4\pi}{3}}\,Y_{10}$, Eq. (32) will become

$$\boldsymbol{\varepsilon}_\lambda \cdot \boldsymbol{r} = \sqrt{\frac{4\pi}{3}}\,r\left(\frac{-\varepsilon_{x\lambda} + i\varepsilon_{y\lambda}}{\sqrt{2}}Y_{11} + \frac{\varepsilon_{x\lambda} + i\varepsilon_{y\lambda}}{\sqrt{2}}Y_{1-1} + \varepsilon_{z\lambda}Y_{10}\right) \quad (33)$$

That leads to

$$\boldsymbol{\varepsilon}_\lambda \cdot < \psi_f|\boldsymbol{r}|\psi_i = \sqrt{\frac{4\pi}{3}}\int_0^\infty r^3 R^*_{nf,lf}\, R_{ni,li} dr$$

$$\times \int Y^*_{lf,mf}\,(\frac{-\varepsilon_{x\lambda}+i\varepsilon_{y\lambda}}{\sqrt{2}}Y_{11} + \frac{\varepsilon_{x\lambda}+i\varepsilon_{y\lambda}}{\sqrt{2}}Y_{1-1} + \varepsilon_{z\lambda}Y_{10})Y_{li,mi}d\Omega \qquad (34)$$

The integration over the angular degree of freedom can be calculated using Wigner-Eckart theorem

$$\int Y^*_{lf,mf}\left(\frac{-\varepsilon_{x\lambda}+i\varepsilon_{y\lambda}}{\sqrt{2}}Y_{11} + \frac{\varepsilon_{x\lambda}+i\varepsilon_{y\lambda}}{\sqrt{2}}Y_{1-1} + \varepsilon_{z\lambda}Y_{10}\right)Y_{li,mi}d\Omega =< l_f, m_f|Y_{l,m'}|l_i, m_i >$$

$$= \sqrt{\frac{3(2l_i+1)}{4\pi(2l_f+1)}} < l_i, 1; 0,0|l_f, 0 > < l_i, 1; m_i, m'|l_f, m_f > \qquad (35)$$

Where the value of $m' = -1, 0, 1$. Thus, by substituting Eq. (35) into Eqs. (30) & (31), we get

$$W^{emi} \sim \; < l_i, 1; m_i, m'|l_f, m_f >^2 \qquad (36)$$

And

$$W^{abs} \sim \; < l_i, 1; m_i, m'|l_f, m_f >^2 \qquad (37)$$

The dipole selection rules are similar to that specified by the selection rules of the Clebsch–Gordan coefficient $<l_i, 1; m_i, m'|l_f, m_f >$. Thus

- Transition rates are zero unless $m_f - m_i = m' = -1, 0, 1$.
- Allowed values of l_f are $l_i - 1 \leq l_f \leq l_i + 1$ *i.e.* $l_f - l_i = -1, 0, 1$. Since Clebsch–Gordan coefficient $<l_i, 1; m_i, m'|l_f, m_f >$ is zero for $l_i = l_f = 0$. This implies that no transition between $l_i = 0$ and $l_f = 0$.
- Finally, since the coefficient $<l_i, 1; 0,0|l_f, 0 >$ vanishes unless $(-1)^{l_i - l_f + 1} = 1$ or $(-1)^{l_i - l_f} = -1$, then $(l_i - l_f)$ must be an odd integer i.e. $l_i - l_f$ = odd integer. This signifies that in case of electric dipole transitions, the final and initial states must have different parities. For example, $1s \rightarrow 2s, 2p \rightarrow 3p, etc.$ are forbidden, while transitions like $1s \rightarrow 2p, 2p \rightarrow 3s$, etc. are allowed.

SPONTANEOUS EMISSION

The rate of emission of photon from atom in case of quantized radiation is

$$W^{emi} = \frac{4\pi^2 e^2 \omega_{fi}^2}{m^2 V \omega_k}\left(n_{\lambda,\boldsymbol{k}} + 1\right)\left|\boldsymbol{\varepsilon}^*{}_\lambda \cdot < \psi_f|\boldsymbol{r}|\psi_i >\right|^2 \delta\left(E_f - E_i + \hbar\omega_k\right)$$

The expression shows that transition rate does not vanish even if $n_{\lambda,k} = 0$ (external radiation field) i.e. no perturbation is applied. The transition rate for spontaneous emission are

$$W^{emi} = \frac{4\pi^2 \omega_{fi}^2}{m^2 V \omega_k} n_{\lambda,\boldsymbol{k}}\left|\boldsymbol{\varepsilon}^*{}_\lambda \cdot < \psi_f|e\boldsymbol{r}|\psi_i >\right|^2 \delta\left(E_f - E_i + \hbar\omega_k\right)$$

$$= \frac{4\pi^2 \omega_{fi}^2}{m^2 V \omega_k} n_{\lambda,\boldsymbol{k}}\left|\boldsymbol{\varepsilon}^*{}_\lambda \cdot \boldsymbol{d_{fi}}\right|^2 \delta\left(E_f - E_i + \hbar\omega_k\right) \qquad (38)$$

Where $\boldsymbol{d} = -e\boldsymbol{r}$ is electron electric dipole and

$$\boldsymbol{d_{fi}} = <\psi_f|\boldsymbol{d}|\psi_i> = <\psi_f|e\boldsymbol{r}|\psi_i> \tag{39}$$

The transition rate corresponding to the transition of the atom from the initial state $|\psi_i>$ to the final state $|\psi_f>$ as a result of its spontaneous emission of a photon of energy $\hbar\omega_k$. The final states of the system consist of products of discrete atomic states and a continuum of photonic states. The photon emitted will be detected in general as having a momentum in the momentum interval $(p, p+dp)$ located around $p = \hbar k$. The transition rate needs then to be summed over the continuum of the final photonic states. The number of final photonic states within the unit volume V, whose momenta are within the interval $(p, p+dp)$, is given by

$$d^3n = \frac{Vd^3p}{(2\pi\hbar)^3} = \frac{Vp^2dpd\Omega}{(2\pi\hbar)^3} = \frac{V\hbar^3\omega^2}{(2\pi\hbar)^3c^3}d\Omega d\omega = \frac{V\omega^2}{(2\pi c)^3}d\Omega d\omega \tag{40}$$

The transition rate corresponding to the emission of a photon in the solid angle $d\Omega$ is obtained by integrating of transition rate over dω:

$$d\Gamma^{emi} = \frac{V}{(2\pi c)^3}d\Omega\int\omega^2 W^{emi}d\omega = \frac{1}{2\pi c^3}d\Omega\left|\boldsymbol{\varepsilon}^*{}_\lambda\cdot\boldsymbol{d_{fi}}\right|^2\int\omega_{fi}^2\,\omega\delta\left(E_f - E_i + \hbar\omega\right)d\omega$$

$$= \frac{1}{2\pi\hbar c^3}d\Omega\left|\boldsymbol{\varepsilon}^*{}_\lambda\cdot\boldsymbol{d_{fi}}\right|^2\int\omega_{fi}^2\,\omega\delta\left(\omega_{if} - \hbar\omega\right)d\omega \tag{41}$$

Here we used $\delta\left(E_f - E_i + \hbar\omega\right) = \frac{1}{\hbar}\,\delta\left(\omega_{if} - \hbar\omega\right)$ with $\omega_{if} = \frac{E_i - E_f}{\hbar}$. The integration of Eq. (41) gives

$$d\Gamma^{emi} = \frac{\omega^3}{2\pi\hbar c^3}\left|\boldsymbol{\varepsilon}^*{}_\lambda\cdot\boldsymbol{d_{fi}}\right|^2 d\Omega \tag{42}$$

Let the emitted photon travels along $\boldsymbol{k} = k\,\boldsymbol{\hat{n}}$ that is normal to $\boldsymbol{\varepsilon}^*{}_\lambda$(corresponds to specific state of polarization). To obtain transition rate corresponding to any state of polarization, we need to sum over two state of polarization of the photon i.e.

$$\sum_{\lambda=1}^{2}\left|\boldsymbol{\varepsilon}^*{}_\lambda\cdot\boldsymbol{d_{fi}}\right|^2 = \left|\varepsilon^*{}_1(d_{fi})_1\right|^2 + \left|\varepsilon^*{}_2(d_{fi})_2\right|^2 = \left|d_{fi}\right|^2 - \left|(d_{fi})_3\right|^2 \tag{43}$$

Since $\boldsymbol{d_{fi}}$ is matrix elements and hence symmetric in all directions. Thus

$$<\left|(d_{fi})_1\right|^2> = <\left|(d_{fi})_2\right|^2> = <\left|(d_{fi})_3\right|^2> = \frac{1}{3}<\left|d_{fi}\right|^2> \tag{44}$$

Thus, an average over polarization

$$\sum_{\lambda=1}^{2}\left|\boldsymbol{\varepsilon}^*{}_\lambda\cdot\boldsymbol{d_{fi}}\right|^2 = \left|d_{fi}\right|^2 - \frac{1}{3}<\left|d_{fi}\right|^2> = \frac{2}{3}<\left|d_{fi}\right|^2> \tag{45}$$

Using Eq. (45), we obtain transition rate as

$$d\Gamma^{emi} = \frac{\omega^3}{3\pi\hbar c^3}\left|\boldsymbol{d_{fi}}\right|^2 d\Omega \tag{46}$$

We integrate over the angular part of the degree of freedom only and not over all possible directions that gives $\int d\Omega = 4\pi$. Thus, transition rate will be

$$\Gamma^{emi} = \frac{4\omega^3}{3\hbar c^3}\left|\boldsymbol{d_{fi}}\right|^2 = \frac{4\omega^3 e^2}{3\hbar c^3}\left|< \psi_f|\boldsymbol{r}|\psi_i >\right|^2 \tag{47}$$

Where $\omega = \frac{E_f - E_i}{\hbar}$.

We obtain total power (intensity) of radiated by the electron as $I = \hbar\omega\Gamma^{emi}$. Thus,

$$I = \frac{4\omega^4 e^2}{3c^3}\left|< \psi_f|\boldsymbol{r}|\psi_i >\right|^2 \tag{48}$$

Eq. (47) & (48) give the transition rate and intensity for single electron-atom system. For a system having z number of electrons, the dipole moment will be

$$\boldsymbol{d} = -e\sum_{j=1}^{2}\boldsymbol{r_j} \tag{49}$$

The average lifetime of an excited state is given as

$$\tau = \frac{1}{\sum_f \Gamma_{i\to f}^{emi}} = \frac{1}{\Gamma^{emi}} \tag{50}$$

Reference:

1) Quantum Mechanics Concepts and Applications by Nouredine Zettili
2) A Text Book of Quantum Mechanics by P.M. Mathews and K.Venkatesan
3) Quantum Mechanics by L.I. Schiff