Semi-classical theory of radiation

by

Dr. R. S. Singh

Prof. (Physics)

Govt. V.Y.T.PG Autonomous College, Durg (C.G.)-491001

Semi-classical theory of radiation

In the semi-classical radiation theory, atoms of the material particles are treated quantum-mechanically. But the electromagnetic radiation, with which these atoms interact, is treated classically. *That is why, this is called a semi-classical radiation theory*.

The interactions between the particles and the radiation field correspond to interaction terms in the Hamiltonian, which are treated by time-dependent perturbation theory.

Semi-classical radiation theory describes absorption and induced emission, but is insufficient to describe the spontaneous emission of radiation.

The quantum theory of radiation is used to describe the spontaneous emission.

Hamiltonian of the atomic electron (for simplicity, one electron having mass 'm', charge 'e' and spin S), in the absence of external perturbation is given by :

$$H_0 = p^2/2m + V(r)$$

When the electromagnetic radiation having vector potential A(r,t) and scalar potential φ(r,t) is applied on the atom, then due to interaction of electron with the electromagnetic radiation, p and V are modified as :

$p \rightarrow (p - eA/c)$ and $V \rightarrow (V + e\varphi)$

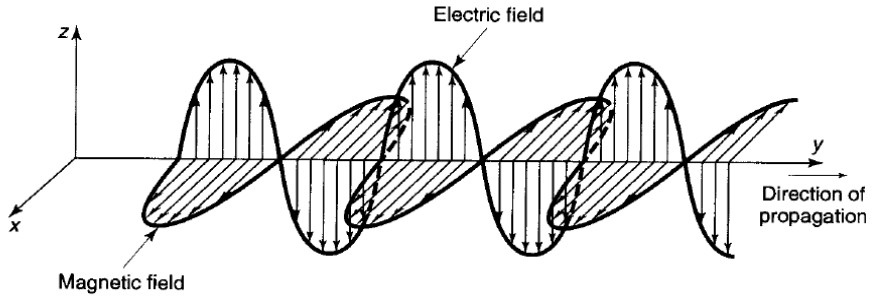
Magnetic field B and electric field E are related to the vector potential A and scalar potential φ by $B = \nabla \times A$ and $E = -\nabla\varphi - (1/c)\,\partial A/\partial t$, respectively.

Hence, the Hamiltonian of the atomic electron in an external electromagnetic field is given by :

$$H = \frac{1}{2m}\left(\mathbf{p} - \frac{e}{c}\mathbf{A}\right)^2 + V(\mathbf{r}) + e\phi - \frac{e}{mc}\mathbf{S}\cdot\mathbf{B}$$

(We have assumed that only one atomic electron is involved in interaction and the nucleus is infinitely large).

$$H = \frac{\mathbf{p}^2}{2m} - \frac{e}{2mc}(\mathbf{p}\cdot\mathbf{A} + \mathbf{A}\cdot\mathbf{p}) + \frac{e^2}{2mc^2}\mathbf{A}^2 + V(\mathbf{r}) + e\phi - \frac{e}{mc}\mathbf{S}\cdot\mathbf{B}$$



Operating **p**·**A** on an arbitrary function $\psi(\mathbf{r})$,

$$(\mathbf{p}\cdot\mathbf{A})\,\psi(\mathbf{r}) = -i\hbar\nabla\cdot\mathbf{A}\,\psi = -i\hbar\,[\mathbf{i}\,\partial/\partial x + \mathbf{j}\,\partial/\partial y + \mathbf{k}\,\partial/\partial z)\cdot\mathbf{A}\,\psi$$

$$= -i\hbar\,[(\partial Ax/\partial x + \partial Ay/\partial y + \partial Az/\partial z)\psi + \mathbf{A}\cdot(\mathbf{i}\,\partial\psi/\partial x + \mathbf{j}\,\partial\psi/\partial y + \mathbf{k}\,\partial\psi/\partial z)]$$

$$= -i\hbar\,[(\nabla\cdot\mathbf{A})\,\psi + \mathbf{A}\cdot\nabla\psi] = -i\hbar\,(\nabla\cdot\mathbf{A})\,\psi + \mathbf{A}\cdot(-i\hbar\nabla)\,\psi$$

$$= -i\hbar\,[(\nabla\cdot\mathbf{A}) + \mathbf{A}\cdot\mathbf{p}]\,\psi$$

Choosing the *Lorentz gauge* $\nabla\cdot\mathbf{A} = 0$ and $\varphi = 0$, we have

$$\mathbf{p}\cdot\mathbf{A} = \mathbf{A}\cdot\mathbf{p}$$

Therefore,

$$H = \mathbf{p}^2/2m - (e/mc)\,\mathbf{A}\cdot\mathbf{p} + (e/2mc^2)\,\mathbf{A}^2 + V(\mathbf{r}) - (e/mc)\,\mathbf{S}\cdot\mathbf{B}$$

$$= H_0 + H'(t)$$

where, $H_0 = \mathbf{p}^2/2m + V(r)$ *is the unperturbed 'atomic' Hamiltonian and*

$H'(t) = -(e/mc)\,\mathbf{A}\cdot\mathbf{p} + (e^2/2mc^2)\,\mathbf{A}^2 - (e/mc)\,\mathbf{B}\cdot\mathbf{S}$

is the time dependent perturbation term.

For a semi classical treatment of radiation, the term A^2 (being small) is ignored.

Hence, the small perturbation, in the low intensity limit, is

$H'(t) = -(e/mc)\,\mathbf{A}\cdot\mathbf{p} - (e/mc)\,\mathbf{B}\cdot\mathbf{S}$

For a plane electromagnetic wave of frequency $\omega = ck$, the time dependence of

A (**r**,t) is

$$\mathbf{A}\,(\mathbf{r},t) = 2\,|\mathbf{A_0}|\,\boldsymbol{\varepsilon}\cos(\mathbf{k}.\mathbf{r} - \omega t)$$

$$= A_0\,\boldsymbol{\varepsilon}\exp[(i\mathbf{k}.\mathbf{r} - i\omega t)] + A^*_0\,\boldsymbol{\varepsilon}\exp[-(i\mathbf{k}.\mathbf{r} - i\omega t)]$$

The Coulomb gauge condition $\nabla\cdot A = 0$ yields $k\cdot A_0 = 0$ i.e. A(r,t) lies in a plane perpendicular to the wave's direction of propagation.

The electric E(r,t) magnetic field B(r,t) associated with the vector potential A (r,t) are given by

$$\vec{E}(\vec{r},t) = -\frac{1}{c}\frac{\partial\vec{A}}{\partial t} = \frac{i\omega}{c}A_0\vec{\varepsilon}\left[-e^{i(\vec{k}\cdot\vec{r}-\omega t)} + e^{-i(\vec{k}\cdot\vec{r}-\omega t)}\right],$$

$$\vec{B}(\vec{r},t) = \vec{\nabla}\times\vec{A} = i(\vec{k}\times\vec{\varepsilon})A_0\left[-e^{i(\vec{k}\cdot\vec{r}-\omega t)} + e^{-i(\vec{k}\cdot\vec{r}-\omega t)}\right] = \vec{n}\times\vec{E}$$

[since **k** = k **n** = (ω/c) **n**]

These two relations show that **E** and **B** have same magnitude |**E**| = |**B**|.

Energy density for a single photon of the incident radiation is given by

$$u = \frac{1}{8\pi}(|\vec{E}|^2 + |\vec{B}|^2) = \frac{1}{4\pi}|\vec{E}|^2 = \frac{\omega^2}{\pi c^2}|A_0|^2 \sin^2(\vec{k}\cdot\vec{r} - \omega t)$$

Averaging this expression over time, we see that the energy of a single photon per unit volume, $\hbar\omega/V$, is given by $(\omega^2/2\pi c^2)|A_0|^2 = \hbar\omega/V$ and hence $|A_0|^2 = 2\pi\hbar c^2/(\omega V)$, which, when put into the above equation for **A** (**r**,t) gives

$$\vec{A}(\vec{r}, t) = \sqrt{\frac{2\pi\hbar c^2}{\omega V}}\left[e^{i(\vec{k}\cdot\vec{r}-\omega t)} + e^{-i(\vec{k}\cdot\vec{r}-\omega t)}\right]\vec{\varepsilon}$$

This gives

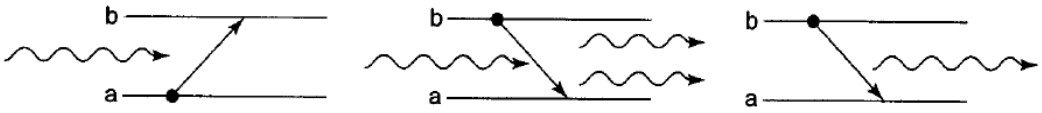
H′(t) = - (e/mc) **A**(**r,**t)·**p** – (e/mc) **B**·**S**

= - (e/mc) $(2\pi\hbar c^2/\omega V)^{1/2}$ **ε**·**p**[exp (i**k.r** - iωt) + exp (- i**k.r** + iωt)] – (e/mc) **B**·**S**

Thus, the interaction of an atomic electron with radiation has the structure of harmonic perturbation. The term exp (-iωt) gives rise to **absorption** of incident photon of energy ħω by the atom *i.e. absorption occurs when the atom receives a photon from radiation;* and exp (iωt) to **stimulated emission** of a photon of energy ħω by the atom, *which occurs when radiation gains a photon from decaying atom*.

In stimulated emission, one starts with one (incident) photon & ends up with two – incident photon plus the photon given up by the atom resulting from transition of atom from higher to lower energy level.

When there are large no. of atoms in the same excited state, a single external photon triggers an avalanche of photons (LASER).



(a) Absorption (b) Stimulated emission (c) Spontaneous emission

Classical treatment do not account for 'spontaneous emission', which occurs even in the absence of external perturbing field. Spontaneous emission *is a purely quantum effect.*

Considering the small time dependent perturbation H′, if the system is initially in state |i> and the perturbation is turned on at t = 0, the first order perturbation amplitude for finding the system in state |f> at t > 0 is given by

$$a_{fi}^{(1)}(t) = \frac{1}{i\hbar}\int_0^t e^{\omega_{fi}it'}\langle f|H'(t')|i\rangle\, dt' = \frac{ie}{mc\hbar}\int_0^t e^{i\omega_{fi}t'}\langle f|\mathbf{A}(\mathbf{r}, t)\cdot\mathbf{p} + \mathbf{S}\cdot[\nabla\times\mathbf{A}(\mathbf{r}, t)]|i\rangle\, dt'$$

with ħω = E_f – E_i. Integrating over dt′, we obtain

$$a_{fi}^{(1)}(t) = \frac{ie}{mc\hbar}\int_0^t \left\{ e^{i(\omega_{fi}-\omega)t'} \langle f | \mathbf{A}_0 e^{i\mathbf{k}\cdot\mathbf{r}} [\hat{\boldsymbol{\varepsilon}} \cdot \mathbf{p} + i\mathbf{S}\cdot(\mathbf{k}\times\hat{\boldsymbol{\varepsilon}})] | i \rangle \right.$$

$$\left. + e^{i(\omega_{fi}+\omega)t'} \langle f | \mathbf{A}_0^* e^{-i\mathbf{k}\cdot\mathbf{r}} [\hat{\boldsymbol{\varepsilon}} \cdot \mathbf{p} - i\mathbf{S}\cdot(\mathbf{k}\times\hat{\boldsymbol{\varepsilon}})] | i \rangle \right\} dt'$$

Therefore,

$$a_{fi}^{(1)}(t) = -\frac{e^{i(\omega_{fi}-\omega)t}-1}{\omega_{fi}-\omega}\frac{T_{fi}^{+}}{\hbar} - \frac{e^{i(\omega_{fi}+\omega)t}-1}{\omega_{fi}+\omega}\frac{T_{fi}^{-}}{\hbar}$$

where we define

$$\begin{cases} T_{fi}^{+} \equiv -\dfrac{e}{mc}\langle f | e^{i\mathbf{k}\cdot\mathbf{r}} A_0 [\hat{\boldsymbol{\varepsilon}} \cdot \mathbf{p} + i\mathbf{S}\cdot(\mathbf{k}\times\hat{\boldsymbol{\varepsilon}})] | i \rangle \\ T_{fi}^{-} \equiv -\dfrac{e}{mc}\langle f | e^{-i\mathbf{k}\cdot\mathbf{r}} A_0^* [\hat{\boldsymbol{\varepsilon}} \cdot \mathbf{p} - i\mathbf{S}\cdot(\mathbf{k}\times\hat{\boldsymbol{\varepsilon}})] | i \rangle \end{cases}$$

Here $T_{fi}^{\pm}$ are the transition matrices and have the matrix elements for a one-electron system in a linearly polarized radiation field as

$$T_{fi}^{\pm} \equiv -(e/mc) \langle f | e^{ik\cdot r} \mathbf{A_0}[\boldsymbol{\varepsilon}\cdot\mathbf{p} \pm i\mathbf{S}\cdot(\mathbf{k}\times\boldsymbol{\varepsilon})] | i \rangle$$

Since, $(e^{i\theta}-1)/\theta = (e^{i\theta/2}e^{i\theta/2} - e^{i\theta/2}e^{-i\theta/2})/\theta$

$$= 2i\, e^{i\theta/2} \sin(\theta/2)]/\theta$$

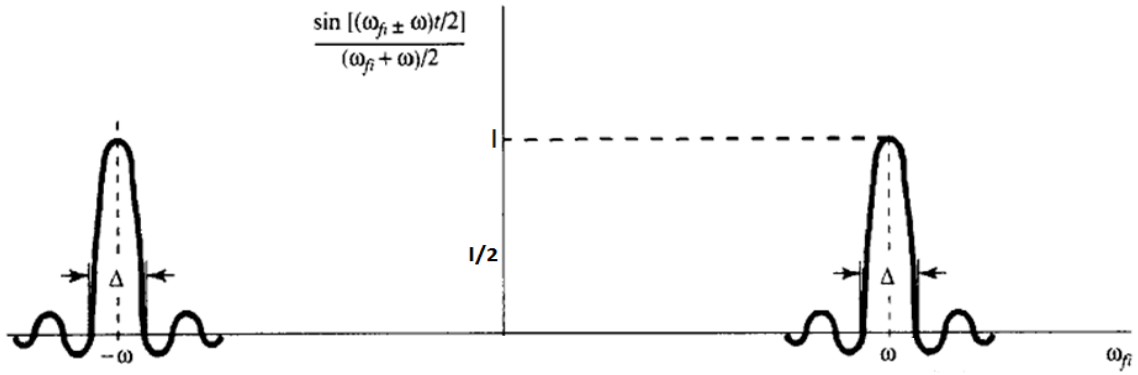
$$= [i\, e^{i\theta/2} \sin(\theta/2)] / (\theta/2)$$

we have

$$\frac{e^{i(\omega_{fi}\pm\omega)t}-1}{\omega_{fi}\pm\omega} = ie^{i(\omega_{fi}\pm\omega)/2}\frac{\sin[(\omega_{fi}\pm\omega)t/2]}{(\omega_{fi}\pm\omega)/2}$$

Therefore, the transition amplitude

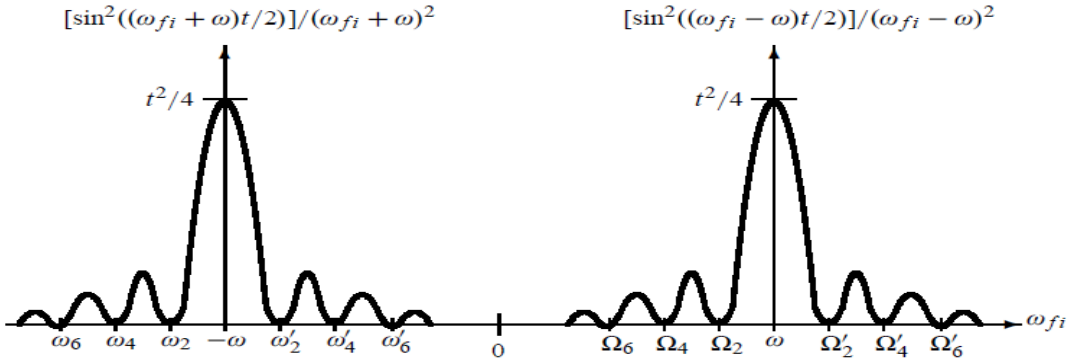
$$a_{fi}^{(1)}(t) = i\, e^{i(\omega fi \pm \omega)/2} \sin[\{(\omega_{fi} \pm \omega)t/2\}/(\omega_{fi} \pm \omega)/2]\, T_{fi}^{\pm}/\hbar$$



Transition probability $P_{fi}(t) = |a_{fi}^{(1)}(t)|^2$

At resonance *i.e. at* $\omega = \pm \omega_{fi}$:

$$P_{fi}^{\pm}(t) = |T_{fi}^{\pm}|^2/\hbar^2 \{\sin [\{(\omega_{fi} \pm \omega)t/2\}/(\omega_{fi} \pm \omega)/2]\}^2$$



Transition probability is an oscillating sinusoidal function with a period $2\pi/\omega_{fi}$. It has an interference pattern and decays rapidly as ω moves away from $\omega = \pm \omega_{fi}$. The height and width of the main peak are proportional to t^2 and $1/t$; *'t', being the interaction-time of electron with the radiation field i. e. time during which e.m. field is on*.

Transition peaks are maximum either at $\omega_{fi} = -\omega$ or at $\omega_{fi} = \omega$ i.e. probability of transition is maximum when the frequency of perturbing field $\omega = \pm \omega_{fi}$.

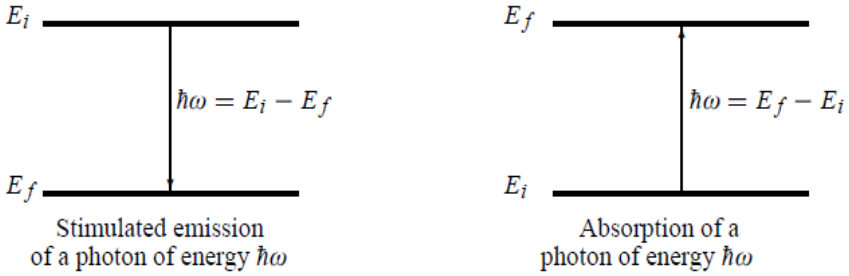
i. ***Absorption*** $(\omega_{fi} > 0)$:

$$P_{fi}(t) \cong \frac{|T_{fi}^{+}|^2}{\hbar^2} \left\{ \frac{\sin [(\omega_{fi} - \omega) t/2]}{(\omega_{fi} - \omega)/2} \right\}^2$$

ii. ***Induced emission*** $(\omega_{fi} < 0)$:

$$P_{fi}(t) \cong \frac{|T_{fi}^{-}|^2}{\hbar^2} \left\{ \frac{\sin [(\omega_{fi} + \omega) t/2]}{(\omega_{fi} + \omega)/2} \right\}^2$$

Line Width : It is the width of the main peak at half of the maximum intensity. *Its quantum analogue is initial transition probability per unit time for spontaneous emission.*



Thus, the effect of time dependent perturbation of the quantum system is to absorb *or emit* radiation quantum (photon) by *or from* the system as a result of electronic transition.

For a strictly monochromatic field, these transition probabilities depend strongly on the difference $\omega - |\omega_{fi}|$, and lead to a nonstationary transition rate. A transition probability that is linear in time (constant transition rate) is obtained if one considers the transition from an initial state $|i\rangle$ to a continuum of final states $|f\rangle$. In this case, the transition rate is obtained by using a *Fermi golden rule:*

$$W_{fi}^{\pm} = \frac{dP^{\pm}(t)}{dt} = \frac{2\pi}{\hbar}|\langle f|T^{\pm}|i\rangle|^2 \rho(E_f = E_i \pm \hbar\omega)$$

where $\rho(E_f)$ is the density of the final states. Similarly, when the radiation field is not monochromatic, but rather contains a spectrum of frequencies $u(\omega)$, the transition rate is

$$W_{fi} = \frac{4\pi^2 e^2}{m^2\hbar^2}\frac{u(\omega_{fi})}{\omega_{fi}^2}\langle f|e^{\pm i\mathbf{k}\cdot\mathbf{r}}[\hat{\boldsymbol{\varepsilon}}\cdot\mathbf{p} \pm i\mathbf{S}\cdot(\mathbf{k}\times\hat{\boldsymbol{\varepsilon}})]|i\rangle|^2$$

where $|i\rangle$ and $|f\rangle$ are the initial and final (discrete) states, and the plus/minus signs correspond to absorption and induced emission, respectively.

MULTIPOLE TRANSITIONS

In the long wavelength approximation, $e^{\pm i\mathbf{k}\cdot\mathbf{r}} \approx 1 + i\mathbf{k}\cdot\mathbf{r}\cdots$ so $T_{fi}^{\pm}$ is given by the following multipole expansion:

$$T_{fi}^{\pm} \approx im\omega_{fi}\langle f|\hat{\boldsymbol{\varepsilon}}\cdot\mathbf{r}|i\rangle + \frac{i}{2}\langle f|(\mathbf{L}+2\mathbf{S})\cdot(\mathbf{k}\times\hat{\boldsymbol{\varepsilon}})|i\rangle - \frac{m\omega_{fi}}{2}\langle f|(\mathbf{k}\cdot\mathbf{r})(\hat{\boldsymbol{\varepsilon}}\cdot\mathbf{r})|i\rangle$$

The first term corresponds to an *electric-dipole transition.* The second term corresponds to a *magnetic-dipole transition,* and the third term corresponds to an *electric-quadrupole transition.* Usually, the transition rate is dominated by the electric-dipole term; in this case the transition rate is

$$W_{fi} = \frac{4\pi^2 e^2}{\hbar^2}u(\omega_{fi})|\langle f|\hat{\boldsymbol{\varepsilon}}\cdot\mathbf{r}|i\rangle|^2$$

However, for particular states $|i\rangle$ and $|f\rangle$, $\langle f|\hat{\boldsymbol{\varepsilon}}\cdot\mathbf{r}|i\rangle$ may vanish. This state is called the *forbidden transition.* Note that for an isotropic external radiation field, the polarization vector $\boldsymbol{\varepsilon}$ is randomly oriented. Averaging the components of the unit vector $\hat{\boldsymbol{\varepsilon}}$ over all angles gives

$$W_{fi} = \frac{4\pi^2 e^2}{3\hbar^2}u(\omega_{fi})|\langle f|\mathbf{r}|i\rangle|^2 \equiv B_{fi}u(u_{fi})$$

B_{fi} are known as the *Einstein coefficients* for absorption and induced emission.

SPONTANEOUS EMISSION

An excited atomic system can also emit radiation in the absence of an external radiation field. The transition rate for a spontaneous transition, in the dipole approximation, is given by

$$W_{fi}^{\text{spon}} = \frac{4}{3}\frac{e^2}{\hbar}\frac{\omega_{fi}^3}{c^3}|\langle f|r|i\rangle|^2 \equiv A_{fi}$$

where A_{fi} is the Einstein coefficient for spontaneous emission.

Electric-dipole transitions: To obtain the selection rules for electric-dipole transitions we consider matrix elements of the form $\langle f|x|i\rangle$, $\langle f|y|i\rangle$, and $\langle f|z|i\rangle$ where $|i\rangle$ and $|f\rangle$ are eigenstates of an electron moving in a central potential. The unperturbed wave function is then given by

$$\begin{cases} |i\rangle \equiv |n_i, l_i, m_i\rangle \rightarrow \psi_{n_i l_i m_i} = R_{n_i l_i}Y_{l_i}^{m_i}(\theta,\phi) \\ |f\rangle \equiv |n_f, l_f, m_f\rangle \rightarrow \psi_{n_f l_f m_f} = R_{n_f l_f}Y_{l_f}^{m_f}(\theta,\phi) \end{cases}$$

where $Y_l^m(\theta, \phi)$ are the spherical harmonic functions. In this representation,

$$\begin{cases} x \pm iy = r \sin\theta e^{\pm i\phi} = \mp\sqrt{\dfrac{8\pi}{3}} r Y_1^{\pm 1}(\theta, \phi) \\ z = r\cos\theta = \sqrt{\dfrac{4\pi}{3}} r Y_1^0(\theta) \end{cases}$$

Therefore, the matrix element $\langle f|z|i\rangle$ is proportional to the angular integral

$$\int \left(Y_{l_f}^{m_f}\right)^* (\theta, \phi)\, Y_1^0(\theta) Y_{l_i}^{m_i}(\theta, \phi)\, d\Omega$$

which is different from zero only if $\Delta l = l_f - l_i = \pm 1$ and $\Delta m = m_f - m_i = 0$. Similarly, the matrix elements $\langle f|x|i\rangle$ and $\langle f|y|i\rangle$ are proportional to linear combinations of the form

$$\int \left(Y_{l_f}^{m_f}\right)^* (\theta, \phi) Y_1^{\pm 1}(\theta) Y_{l_i}^{m_i}(\theta, \phi)\, d\Omega$$

which are different from zero only if $\Delta l = \pm 1$ and $\Delta m = \pm 1$. Grouping these results together we finally obtain

$$\begin{cases} \Delta l = l_f - l_i = \pm 1 \\ \Delta m = m_f - m_i = 0, \pm 1 \end{cases}$$

Einstein "*A* coefficient" – Spontaneous Emission

$B_{m\to n}$, $B_{n\to m}$ Einstein *B* Coefficients

induced emission

absorption

$A_{m\to n}$ spontaneous emission coefficient

N_m = number of systems (molecules) in state of energy E_m (upper state)

N_n = number of systems (molecules) in state of energy E_n (lower state)

At temp *T*, Boltzmann law gives:

$$\frac{N_m}{N_n} = \frac{e^{-E_m/k_BT}}{e^{-E_n/k_BT}} = e^{-h\nu_{mn}/k_BT}$$

At equilibrium :

rate of downward transitions = rate of upward transitions

$$N_m\left\{A_{m\to n} + B_{m\to n}\rho(\nu_{mn})\right\} = N_n B_{n\to m}\rho(\nu_{mn})$$

spontaneous emission stimulated emission absorption

Using $\frac{N_m}{N_n} = \frac{e^{-E_m/k_BT}}{e^{-E_n/k_BT}} = e^{-h\nu_{mn}/k_BT}$

$$e^{-h\nu_{mn}/k_BT} = \frac{B_{n\to m}\rho(\nu_{mn})}{A_{m\to n} + B_{m\to n}\rho(\nu_{mn})}$$

Solving for $\rho(\nu_{mn})$

$$\rho(\nu_{mn}) = \frac{A_{m\to n}e^{-h\nu_{mn}/k_BT}}{-B_{m\to n}e^{-h\nu_{mn}/k_BT} + B_{n\to m}}$$

$$B_{n\to m} = B_{m\to n}$$

Then:

$$\rho(\nu_{mn}) = \frac{\frac{A_{m\to n}}{B_{m\to n}}}{e^{h\nu_{mn}/k_BT} - 1}$$

Take "sample" to be black body, reasonable approximation.

Planck's distribution formula

$$\rho(\nu_{mn}) = \frac{8\pi h\nu_{mn}^3}{c^3}\frac{1}{e^{h\nu_{mn}/k_BT} - 1}$$

Gives

$$A_{m\to n} = \frac{8\pi h\nu_{mn}^3}{c^3} B_{m\to n}$$

$$A_{m\to n} = \frac{32\pi^3\nu_{mn}^3}{3c^3\hbar}\left|\mu_{mn}\right|^2$$

Spontaneous emission – light not necessary,
$I = 0$, ν^3 dependence.

Spontaneous Emission

ν^3 dependence

No spontaneous emission - NMR

$\nu \cong 10^8$ Hz

Optical spontaneous emission

$\nu \cong 10^{15}$ Hz

Typical optical spontaneous emission time, 10 ns (10^{-8} s).

$$\left(\frac{\nu_{NMR}}{\nu_{optical}}\right)^3 = \left(\frac{10^8}{10^{15}}\right)^3 = 10^{-21}$$

NMR spontaneous emission time – 10^{13} s (>10^5 years).

Longer magnetic dipole transition is much weaker than optical electric dipole transition.

References used :

1. *Quantum Mechanics by L. I. Schiff, Mc-Graw Hill, Kogakusha,*

2. *Quantum Mechanics – Concepts & Applications by Nouredine Zettili &*
3. *Quantum Mechanics by V. K. Thankappan.*

Assignments

1. What is semi-classical theory or radiation ?
2. Write expression for Hamiltonian of the atomic electron in the external electromagnetic field.
3. Obtain expression for the transition probability at resonance in the stimulated emission of radiation.
4. What is line width?
5. What are multipole transitions ? Write the selection rules for electric-dipole transitions.