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Theory of Radiative Processes

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THEORY OF RADIATIVE PROCESSES

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Layout

- Quantum Mechanics: Revisited
- Radiative Processes for isolated atoms
- Transition rates: Semi-classical
- Line-broadening Mechanisms
 - Homogeneous broadening
 - Inhomogeneous broadening
- Transition Cross-section
- Spontaneous Emission Rate

Quantum Mechanics: Revisited

➤ Wave Mechanics

➤ Quantum mechanical systems (such as atoms, molecules, ions etc.) are given by wave function $\psi(r, t)$.

➤ Itself $\psi(r, t)$ has no physical meaning- it allows to calculate the expectation values of all observables of interest.

➤ Measurable quantities are called observable and are represented by hermitian operator \hat{O} . Expectation values is given by

$$\langle \hat{O} \rangle = \int d^3 r \psi^*(r, t) \hat{O} \psi(r, t).$$

➤ Probability

- The probability of finding the system in volume element d^3r is.

$$\psi^*(r, t) \hat{O} \psi(r, t).$$

- If system exist, its probability of being somewhere has to equal 1.

$$\int \psi^*(r, t) \hat{O} \psi(r, t) d^3r = 1$$

$$\int \psi_n^*(r, t) \hat{O} \psi_m(r, t) d^3r = \delta_{nm}$$

The time development of wave function is determined by Schrödinger equation,

$$i\hbar \frac{\partial}{\partial t} \psi (r, t) = H \psi (r, t).$$

H- the Hamiltonian of the system. The energy of the unperturbed system- an atom not interacting with light is

$$H = \frac{P^2}{2m} + V (r)$$

Stationary States

Stationary states of Schrödinger equation are those for which space and time dependence are separated

$$\psi_n(\mathbf{r}, t) = U_n\left(\begin{matrix} \vec{r} \\ \mathbf{r} \end{matrix}\right) e^{-i\omega t}$$

Time independent equation,

$$HU_n\left(\begin{matrix} \vec{r} \\ \mathbf{r} \end{matrix}\right) = E_n U_n\left(\begin{matrix} \vec{r} \\ \mathbf{r} \end{matrix}\right) = \hbar\omega_n U_n\left(\begin{matrix} \vec{r} \\ \mathbf{r} \end{matrix}\right).$$

Eigen functions having same eigen values are normal

$$\int U_n^*(\mathbf{r}) U_m(\mathbf{r}) d\vec{r} = \delta_{nm}$$

Completeness

$$\sum_n U_n^*(r) U_n(r) = 1$$

The wave function

$$\psi(r, t) = \sum_n \psi_n(r, t) = \sum_n C_n(t) U_n(r) e^{-i\omega_n t}$$

$C_n(t)$ - Expansion coefficients

-constant for problems related with free Hamiltonian

-time dependent for interaction Hamiltonian

$$\sum_n |C_n|^2 = 1$$

Gives the probability of finding the system in state n.

$$\langle \hat{O} \rangle = \sum_{n,m} C_n^* C_m e^{-i(\omega_n - \omega_m)t} \hat{O}_{nm}$$

Where

$$O_{nm} = \int d^3r U_n^*(\mathbf{r}) \hat{O} U_m(\mathbf{r})$$

DIRAC'S NOTATION

- **The wave function of wave mechanics corresponds to the state vector of the Dirac's formulation of the quantum mechanics.**
- **The relation between state vector and wave function is analogous to using vectors instead of coordinates.**

A vector \mathbf{V} can be expanded as,

$$\vec{V} = V_x \hat{x} + V_y \hat{y}$$

In Dirac Notation

$$|V\rangle = V_x |x\rangle + V_y |y\rangle$$

X-component of a vector is obtained by

$$\vec{V} \cdot \hat{x} = V_x$$

In Dirac Notation

$$\langle x|V\rangle = V_x \text{ and } \langle y|V\rangle = V_y$$

Using these equations we can write

$$\begin{aligned} |V\rangle &= |x\rangle\langle x|V\rangle + |y\rangle\langle y|V\rangle \\ &= (|x\rangle\langle x| + |y\rangle\langle y|)|V\rangle \\ &\Rightarrow |x\rangle\langle x| + |y\rangle\langle y| = 1 \end{aligned}$$

For n dimensions

$$|V\rangle = \sum_n |n\rangle\langle n|V\rangle \quad \Rightarrow \quad \sum_n |n\rangle\langle n| = I$$

Where $\{|n\rangle\}$ are complete set of vectors- a basis

For continuous basis $\{|r\rangle\}$

$$I = \int d^3 r |\vec{r}\rangle \langle \vec{r}|$$

The wave vector

$$|\psi(t)\rangle = \int d^3 r |\vec{r}\rangle \langle \vec{r}|\psi\rangle$$

Where the wave function

$$\psi(\vec{r}) = \langle \vec{r}|\psi\rangle$$

The expectation value of the operator \hat{O}

$$\langle \hat{O} \rangle = \langle \psi(t) | \hat{O} | \psi(t) \rangle$$

Hermitian

$$\langle \psi(t) | \hat{O} | \psi(t) \rangle = \left[\langle \psi(t) | \hat{O}^\dagger | \psi(t) \rangle \right]^* = \langle \psi(t) | \hat{O} | \psi(t) \rangle^*$$

The set of eigen vectors of a hermitian operator is complete. This means that any arbitrary vector can be expressed as a sum of orthogonal eigen vectors.

$$|\psi\rangle = \sum_{n=0}^{\infty} C_n |x_n\rangle$$

Eigen vectors are orthonormal

$$\langle X_n | X_m \rangle = \delta_{nm}$$

$$\delta_{nm} = 1 \text{ for } n = m$$

$$= 0 \text{ for } n \neq m$$

Completeness relation for discrete case is

$$\sum_n |X_n\rangle\langle X_n| = I$$

The state vector $|\psi\rangle$ in terms of position eigen states (which are continuous).

$$|\psi(t)\rangle = \int d\vec{x} |x\rangle \langle x | \psi \rangle$$
$$\Rightarrow \int d\vec{x} |x\rangle \langle x| = I$$

The normalization of eigen vectors for a continuous set of eigen values is done with the help of dirac delta function

$$\delta(x - x') = 0 \text{ if } x \neq x'$$

$$\delta(x - x') = \infty \text{ if } x = x'$$

$$\langle x | x' \rangle = \delta(x - x')$$

State vectors obey the Schrödinger's equation

$$i\hbar \left| \dot{\psi} \right\rangle = H \left| \psi \right\rangle,$$

$$\left| \psi \right\rangle = \sum_n C_n e^{-i\omega_n t} \left| n \right\rangle$$

Expectation value can be written as

$$\left\langle \psi (t) \left| \hat{O} \right| \psi (t) \right\rangle = \sum_{n,m} C_n^* C_m e^{-i(\omega_n - \omega_m)t} \hat{O}_{nm}$$

where

$$\hat{O}_{nm} = \left\langle m \left| \hat{O} \right| n \right\rangle$$

Two-level Atomic System

Wave function

$$\psi(\vec{r}, t) = C_a U_a(\vec{r}) e^{-i\omega_a t} + C_b U_b(\vec{r}) e^{-i\omega_b t}$$

State vector

$$|\psi\rangle = C_a e^{-i\omega_a t} |a\rangle + C_b e^{-i\omega_b t} |b\rangle$$

Pauli Spin Matrix

Another method to describe two - level atom is a use of 2×2 matrix notation.

The eigen function U_a and U_b or eigen vectors $|a\rangle$ and $|b\rangle$ can be represented by the column vectors.

$$|a\rangle = U_a \leftrightarrow \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$|b\rangle = U_b \leftrightarrow \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

The wave function and wave vector
by the column vectors

$$\psi(\mathbf{r}, t) = \begin{bmatrix} C_a \\ C_b \end{bmatrix}$$

And

$$|\psi(\mathbf{r}, t)\rangle = \begin{bmatrix} C_a \\ C_b \end{bmatrix}$$

The energy and electric dipole operators in terms of Pauli spin matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Spin Flip operators

$$\sigma_+ = \frac{1}{2}(\sigma_x + i\sigma_y) = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$$

$$\sigma_- = \frac{1}{2}(\sigma_x - i\sigma_y) = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

Not hermitian, σ_- flips the system from upper level to lower level

$$\sigma_- \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

While, σ_+ flips the system from lower level to upper level

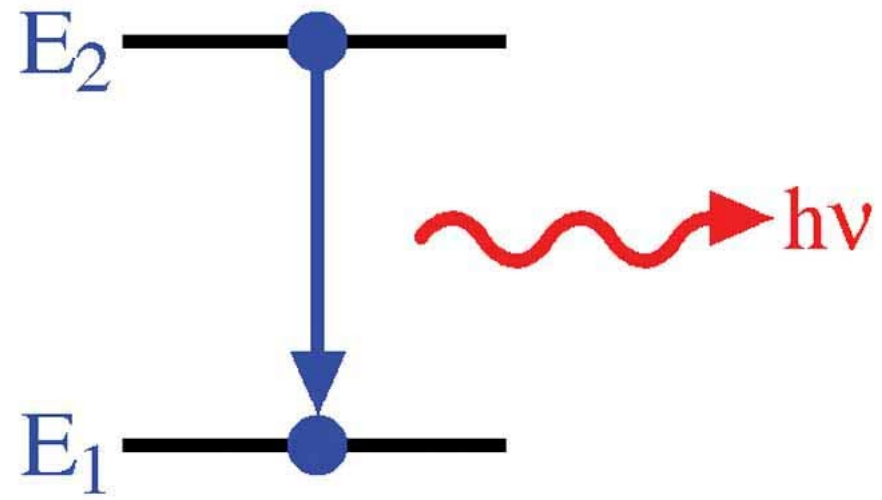
$$\sigma_+ \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

Radiative Processes for Isolated Atoms

Spontaneous Emission

- Atom is in state $|2\rangle$ of given material.
- $E_2 > E_1$ – atom will tend to decay to state $|1\rangle$
- The corresponding energy difference ($E_2 - E_1$) is released by the emission of a photon.

$$\nu = \frac{(E_2 - E_1)}{h}$$



Two possible ways for atom to decay

1. Radiative: Spontaneous emission

2. Non-radiative:

Energy difference

$$E_2 - E_1$$

Is delivered in some other form than electromagnetic radiation e.g. it may go into kinetic energy of the surrounding molecules.

Let N_2 number of atoms in level 2 per unit volume

The rate of decay of these atoms are

$$\left(\frac{dN_2}{dt} \right)_{sp} \propto N_2$$

$$\left(\frac{dN_2}{dt} \right) = -AN_2$$

A- Transition probability for spontaneous emission or Einstein's A coefficient.

$$\tau_{sp} = \frac{1}{A}$$

Radiative wave has no definite phase relationships to that emitted by another atom.

Any direction is possible.

$$N_2 = N_0 e^{-At}$$

N_0 is the initial population .

If population decays to several levels.

$$\begin{aligned}\frac{dN_2}{dt} &= -\left(A_{2i} + A_{2j} + A_{2k} + \dots\right)N_2 \\ &= -\left(\sum_i A_{2i}\right)N_2\end{aligned}$$

The solution is

$$N_2 = N_0 e^{\left\{-\left(\sum_i A_{ui}\right)t\right\}}$$

STIMULATED EMISSION

- Atom is initially in level 2
- An electromagnetic wave of frequency ν given by

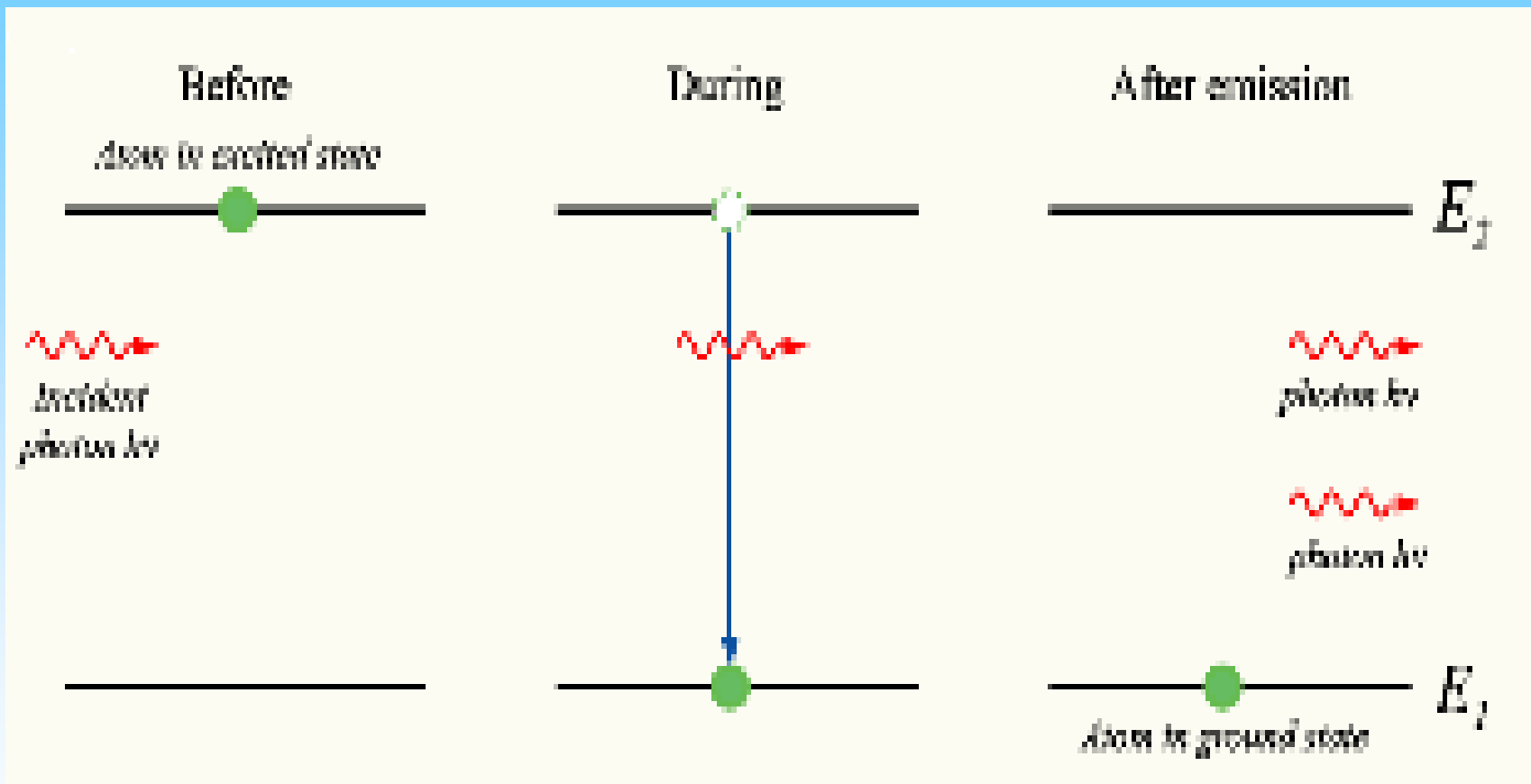
$$E_2 - E_1 = h\nu$$

incident on it.

Finite probability of emission of another in phase photon.

Rate of transition

$$\left(\frac{dN_2}{dt} \right)_{st.em} = -W_{21} N_2$$



W_{21} - stimulated transition probability or rate- (time)⁻¹

W_{21} - depends on intensity of electromagnetic wave.

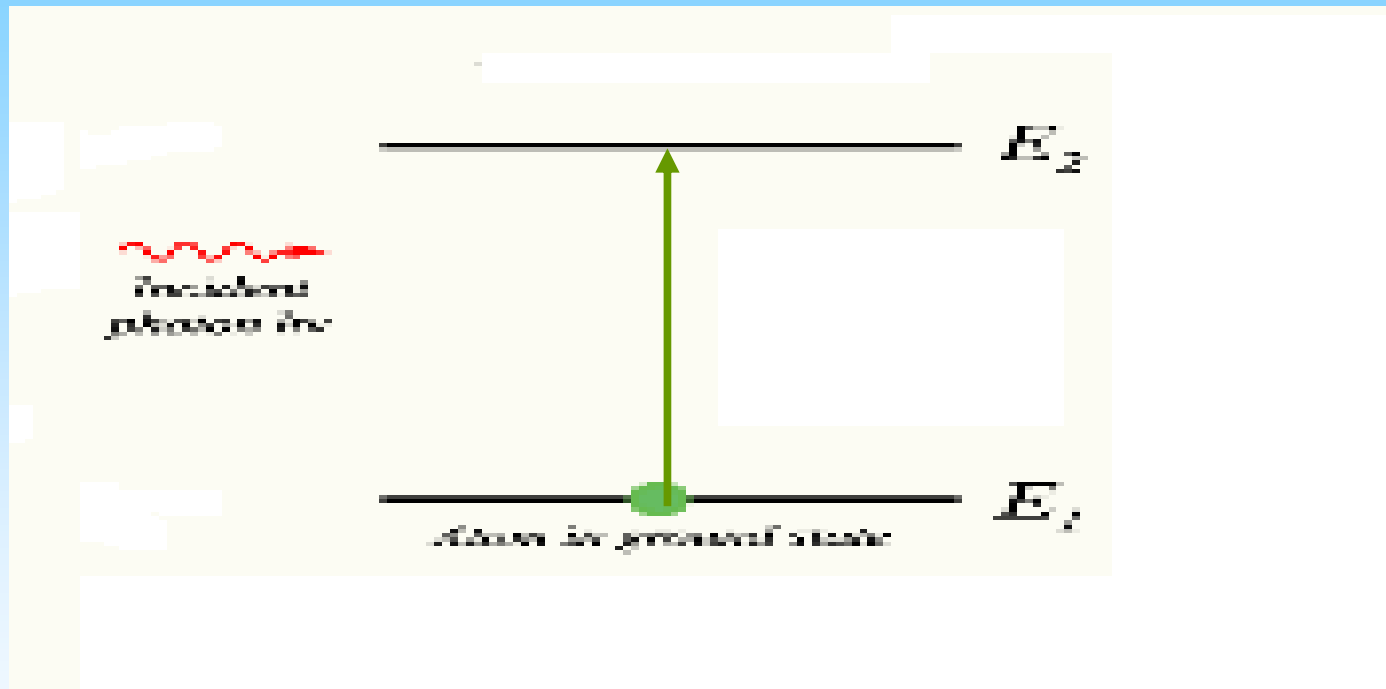
$$W_{21} = \sigma_{21} I (\sigma_{21} F)$$

I (F)- Intensity (Photon flux)

STIMULATED ABSORPTION:

- Atom is in level 1
- Electromagnetic wave of frequency ν incident on the material.
- Finite probability that atom will be raised to level 2.
- Energy of incident wave is absorbed by the atom

Process is called the stimulated absorption.



Stimulated Transition Rate

$$\left(\frac{dN_1}{dt} \right)_{st.ab.} = -W_{12}N_1$$

$$W_{12} = \sigma_{12}F$$

N_1 -number of atoms at a given time lying in level 1

Transition Rates

TRANSITION RATES OF STIMULATED EMISSION AND ABSORPTION

- Semi-classical Theory
- Atom is quantized
- Field is treated classically (using Maxwell's equations)

System: Two-Level Atomic System

$$\psi(r, t) = a_1(t)u_1(r)e^{-iE_1t/\hbar} + a_2(t)u_2(r)e^{-iE_2t/\hbar}$$

$u_1(r)$ & $u_2(r)$ - eigen -function of unperturbed Hamiltonian(H_0).
satisfies time-independent equation.

$$H_0 u_i = E_i u_i$$

$a_1(t)$ - probability amplitudes.

$|a_i(t)|^2$ - probability of finding atoms in state 2.

ω_0 - Transition frequency

$$\omega_0 = \frac{E_2 - E_1}{\hbar} = \omega_{21}$$

- A monochromatic electromagnetic wave incident on atom.
 - Atom acquire an additional energy H' during interaction
- Total Hamiltonian

$$H = H_0 + H'$$

TIME EVOLUTION OF THE SYSTEM

Schrodinger equation

$$i\hbar \frac{\partial \psi(r, t)}{\partial t} = H \psi(r, t)$$

Putting value of $\psi(r,t)$

$$i\hbar \frac{\partial}{\partial t} \left(a_1(t) u_1(r) e^{-iE_1 t / \hbar} \right) + i\hbar \frac{\partial}{\partial t} \left(a_2(t) u_2(r) e^{-iE_2 t / \hbar} \right) = H_0 \left(a_1(t) u_1(r) e^{-iE_1 t / \hbar} + a_2(t) u_2(r) e^{-iE_2 t / \hbar} \right) + H \left(a_1(t) u_1(r) e^{-iE_1 t / \hbar} + a_2(t) u_2(r) e^{-iE_2 t / \hbar} \right)$$

Multiplying with $u_1^*(r)$ and integrating over whole space.

Using

$$\int u_1^*(r) u_1(r) d^3 r = 1$$

$$\int u_i^*(r) H_0 u_i(r) d^3 r = \int E_i u_i^*(r) u_i(r) d^3 r = E_i$$

$$\int u_1^*(r) H_0 u_2(r) d^3 r = \int E_2 u_1^*(r) u_2(r) d^3 r = 0$$

$$\int u_1^*(r) u_2(r) d^3 r = 0$$

$$\int u_1^*(r) H' u_1(r) d^3 r = H'_{11}$$

$$\int u_1^*(r) H' u_2(r) d^3 r = H'_{12}$$

$$\dot{a}_1(t) = \frac{1}{i\hbar} \left(a_1(t) H'_{11} + a_2(t) H'_{12} e^{-i\omega_0 t} \right)$$

Similarly

$$\dot{a}_2(t) = \frac{1}{i\hbar} \left(H'_{21} a_1(t) e^{i\omega_0 t} + a_2(t) H'_{22} \right)$$

INTERACTION HAMILTONIAN:

$$H_I = H_{ED} + H_{EQ} + H_{MD} + H_{NL}$$

H_{ED} -dominates

H' -due to the Interaction of the electric dipole moment of the atom with the electric field of the electromagnetic wave called- **Electric-dipole interaction.**

DIPOLE APPROXIMATION

\vec{r} = vector indicating the electron's position with respect to the nucleus

$$\vec{p} = e\vec{r}$$

ELECTRIC FIELD IN TERMS OF PLANE WAVE

$$\vec{E}(\vec{r}, t) = \epsilon_0 e^{i(k \cdot \vec{r} - \omega t)} + c.c$$

Distance of electron from the nucleus is given by Bohr radius.

$$a_0 \approx 5 \times 10^{-11} m = 0.5 \text{ \AA}$$

\ll Optical wavelength

The spatial variation of the electric field across the dimensions of the atom is very small - neglecting it for long wave-lengths - is called dipole approximation.

$$E(\vec{r}, t) = E_0 e^{-i\omega t} + E_0 e^{i\omega t}$$

$$\approx 2E_0 \cos \omega t$$

$$\cong E_0 \cos \omega t$$

Interaction Hamiltonian

$$H' = 2er \cdot E_0 \cos \omega t$$

Using this

$$\begin{aligned} H'_{12} &= \int u_1^*(r) H' u_2(r) d^3 r \\ &= \int u_1^*(r) e \vec{r} u_2(r) \cdot E_0 \cos \omega t d^3 r \\ &= 2 p_{12} \cdot E_0 \cos \omega t \end{aligned}$$

where

$$p_{12} = \int u_1^*(r) e r u_2(r) d^3 r$$

is the matrix element of electric dipole operator.

Similarly

$$H'_{11} = 2p_{11} \cdot E_0 \cos \omega t$$

$$p_{11} = \int u_1^*(r) e r u_1(r) d^3 r = 0$$

A level does not have a dipole moment.

$e r$ - has odd parity

$u_1^*(r)$ and $u_1(r)$ - has even parity

$$\Rightarrow H'_{11} = H'_{22} = 0$$

Electric dipole transition only occurs between states of opposite parity.

Using these we get

$$\dot{a}_1(t) = \frac{1}{i\hbar} H'_{12} e^{-i\omega_0 t} a_2(t)$$

$$\dot{a}_2(t) = \frac{1}{i\hbar} H'_{21} e^{i\omega_0 t} a_1(t)$$

Two differential equations- can be solved by using initial conditions.

Let at $t=0$, atom is in level 1

$$a_1(0) \cong 1 \quad a_2(0) = 0$$

Assume transition probability is weak--- perturbation analysis can be used.

According to Perturbation theory

$$a_1(t) = a_1^{(0)} + a_1^{(2)} + a_1^{(4)} + \dots$$

$$a_2(t) = a_2^{(1)} + a_2^{(3)} + a_2^{(5)} + \dots$$

As atom is initially in level 1

$$a_1^{(0)} = 1$$

First order corresponds to the probability that atom go to level 2 from level 1.

$$\int_0^t \dot{a}_2(t) dt = \frac{2}{i\hbar} \int_0^t \frac{(p_{21} \cdot E_0)}{2} (e^{i(\omega+\omega_0)t} + e^{-i(\omega-\omega_0)t}) a_1^{(0)} dt$$

Putting value of $a_1^{(0)}$

$$a_2^{(1)} = \frac{1}{i\hbar} (p_{21} \cdot E_0) \left[\frac{e^{i(\omega+\omega_0)t} - 1}{i(\omega + \omega_0)} + \frac{e^{-i(\omega-\omega_0)t} - 1}{-i(\omega - \omega_0)} \right]$$

$\omega \sim$ field frequency and $\omega_0 \sim$ atomic frequency

At resonance

$$\omega \cong \omega_0$$

$(\omega + \omega_0)$ is rapidly oscillating term. Neglecting $e^{i(\omega + \omega_0)t}$

This is called “Rotating wave approximation (RWA)”.

$$a_2^{(1)} = \frac{2 p_{21} \cdot E_0}{\hbar(\omega - \omega_0)} e^{-i(\omega - \omega_0)t/2} \sin \frac{(\omega - \omega_0)t}{2}$$

The second order of $a_1^{(2)}(t)$ is obtained by substituting the value of $a_2^{(1)}(t)$

$$a_1(t) = 1 + |p_{12} \cdot E_0|^2 \times \text{function of time}$$

Then putting this in $\dot{a}_2(t)$, we get the third order of $a_2^{(3)}(t)$

$$a_1(t) = \text{series is even powers of } E_0$$

$$a_2(t) = \text{series is odd powers of } E_0$$

First order is enough for transition rates.

Probability of finding the atom in state 2 is

$$|a_2(t)|^2 = \frac{4|p_{21} \cdot E_0|^2}{\hbar^2} \left(\frac{\sin \Delta\omega t/2}{\Delta\omega} \right)^2$$

Expand

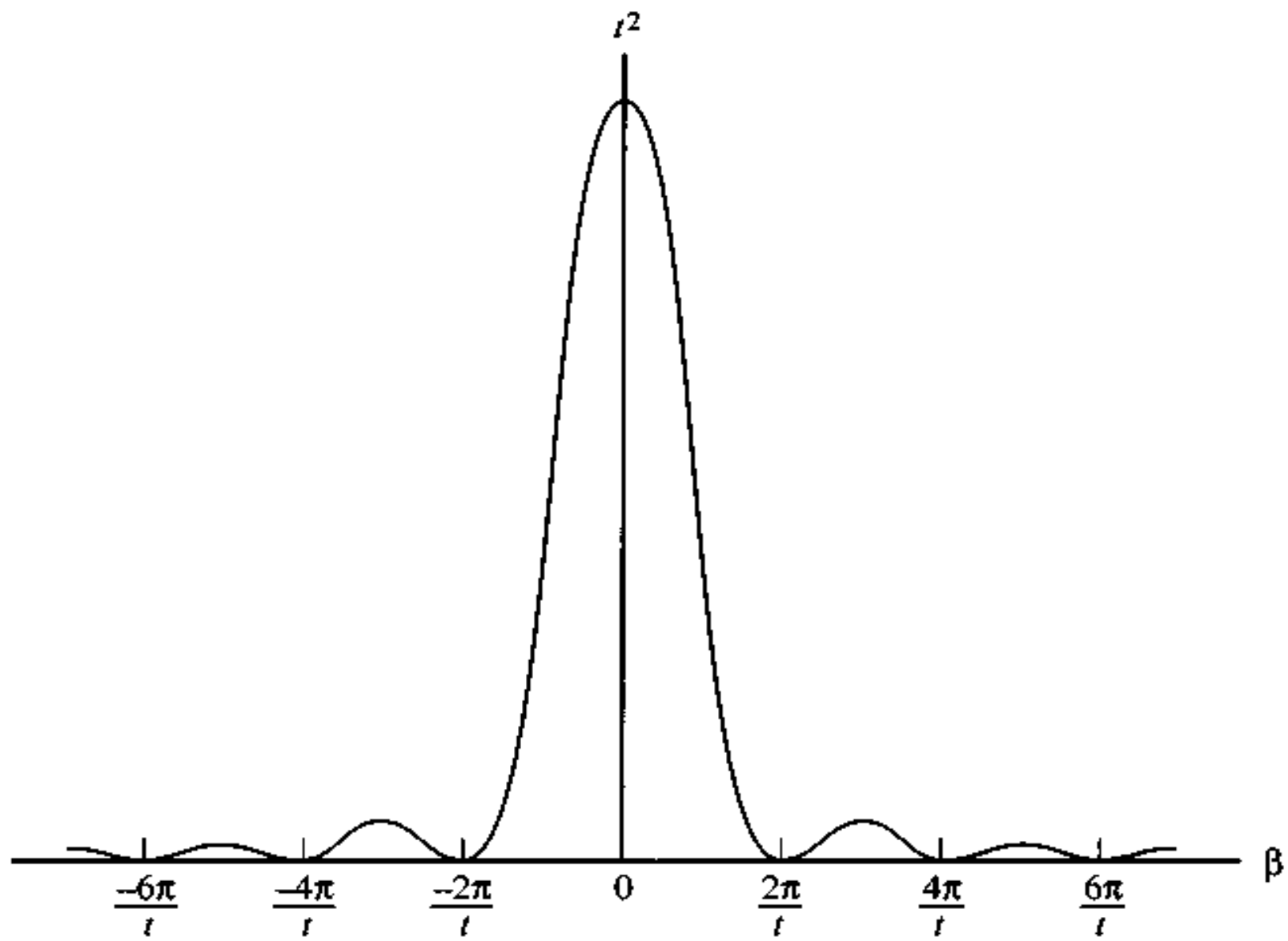
$$\sin \Delta\omega t/2 = \Delta\omega t/2 - \frac{(\Delta\omega t/2)^3}{3!} + \dots$$

$$\frac{\sin \Delta\omega t/2}{\Delta\omega} = \frac{t}{2} - \frac{(\Delta\omega)^2 (t/2)^3}{3!} + \dots$$

For limit $\Delta\omega \rightarrow 0$ $t \propto \infty$

$$\left(\frac{\sin \frac{\Delta\omega t}{2}}{\Delta\omega} \right)^2 \approx \frac{t^2}{4}$$

As t increases, the maximum in the curve moves upwards proportional to t^2 and zeros of the function move in along the horizontal axis towards the origin.



For the area under the curve equal to unity it can be replaced by Dirac delta function with properties

$$\delta(t - t') = \infty \quad t = t'$$

$$\delta(t - t') = 0 \quad t \neq t'$$

$$\left(\frac{\sin \left(\omega - \omega_0 \right) t / 2}{\left(\omega - \omega_0 \right)} \right)^2$$

can be replaced by Dirac delta function $\delta(\omega - \omega_0)$

$$\left(\frac{\sin \Delta \omega t / 2}{\Delta \omega} \right)^2 = \frac{\pi t}{2} \delta(\Delta \omega)$$

Using

$$|a_2(t)|^2 = \frac{2|p_{21} \cdot E_0|^2}{\hbar^2} \pi t \delta(\omega - \omega_0)$$

This is for a single atom.

Electromagnetic wave interact with an ensemble of atoms with randomly oriented dipole moment with respect to field. If θ is the angle between p and E_0 ,

$$|p_{21} \cdot E_0|^2 = E_0^2 |p_{21}|^2 \cos^2 \theta$$

Take average over all the random orientations of dipole moment.

If all angles θ are equally probable, then

$$\langle |p_{21} \cdot E_0|^2 \rangle = E_0^2 |p_{21}|^2 \langle \cos^2 \theta \rangle$$

$$\langle \cos^2 \theta \rangle = \frac{\int_0^\pi \cos^2 \theta \sin \theta d\theta}{\int_0^\pi \sin \theta d\theta}$$

$$\int_0^\pi \sin \theta d\theta = -\cos \theta \Big|_0^\pi = 2$$

$$\int_0^\pi \cos^2 \theta \sin \theta d\theta = ?$$

Putting $\cos\theta = x$ — $\sin\theta d\theta = dx$

$$\int_0^\pi \cos^2\theta \sin\theta d\theta = \int_{-1}^1 x^2 dx = \left. \frac{x^3}{3} \right|_{-1}^1 = \frac{2}{3}$$

$$\langle \cos^2\theta \rangle = \frac{2/3}{2} = \frac{1}{3}$$

$$\Rightarrow \langle |p_{21} \cdot E_0|^2 \rangle = \frac{1}{3} |p_{21}|^2 E_0^2$$

$$|a_0(t)|^2 = \frac{2}{3\hbar^2} |p_{21}|^2 E_0 \pi t \delta(\omega - \omega_0)$$

The energy density of electromagnetic wave is

$$\rho = \frac{n^2 \epsilon_0 E_0^2}{2}$$

$$W_{12} = \frac{4\pi}{3\hbar^2} |p_{21}|^2 \frac{\rho}{n^2 \epsilon_0} \delta(\Delta\omega)$$

$$\text{At } \omega = \omega_0 \quad \delta(\omega - \omega_0) = \infty$$

$$\Rightarrow W_{12} = \infty$$

$$\omega \neq \omega_0 \quad \delta(\omega - \omega_0) = 0$$

$$\Rightarrow W_{12} = 0$$

This is physical unacceptable result

Reason:

- We have assumed that the interaction between the electromagnetic wave and system could continue coherently for an infinite time.
- There are a number of phenomena that prevent the interaction of atom with electromagnetic wave for long time. For example collision, Spontaneous emission.
- Above equations are valid only in time interval between one collision and the next.
- After each collision the relative phase between the atom's wave-function and electric field of the wave undergo a random jump.
- The problem is to find the interaction of atom with a broadband field

W_{12} is valid provided the Dirac delta function - an infinitely sharp function centered at

$$\omega = \omega_0$$

and of unit area such that

$$\int \delta(\omega - \omega_0) d\omega = 1$$

Is replaced by a new function

$$g_t(\omega - \omega_0)$$

again centered at $\omega = \omega_0$, again of unit area.

$$\int g_t(\omega - \omega_0) d\omega = 1$$

but with a finite spectral width.

The shape of function and value of its line width depends Upon the particular broadening mechanism involved.

$$W_{12} = \frac{4\pi}{3\hbar^2} |p_{21}|^2 g_t(\Delta\omega)$$

Stimulated emission rate W_{21} is obtained by changing initial conditions.

$$a_1(0) = 0 \quad \text{and} \quad a_2(0) = 1$$

$$|p_{12}| = |p_{21}| = |p| \quad \text{As} \quad p_{21} = p_{12}^*$$

$$W = W_{12} = W_{21}$$

Line-broadening Mechanisms

• **Line- Broadening Mechanisms**

Broadening

- The term is used to denote the finite spectral width of the response of the atomic systems to the electromagnetic fields.

Two Types of Line Broadening

1. Homogeneous Broadening

2. Inhomogeneous Broadening

Homogeneous Broadening

- Broadening mechanism is homogeneous when it broadens the line of each individual atom and therefore of the whole system in the same way.
- Atoms are indistinguishable
- All atoms have same transition frequency and same energy spectrum
- **Examples:** Collision and Natural Broadening

Inhomogeneous broadening

- A Broadening mechanism is said to be inhomogeneous when it broadens the atomic lines by different amount for different atoms.
- In this case different atoms in an ensemble has different transition frequency and frequencies are distributed over a range.
- **Example:** Doppler Broadening

Collision Broadening

Broadening in Gases

Due to collision of an atom with other atoms, ions, free electrons or the walls of the container.

Broadening in Solids

Due to the interaction of with the phonons of the lattice

- It leads to the change of relative phase between atomic dipole moment and that of a incident wave
- Collision interrupt the process of coherent interaction between the atom and the incident wave
- Atom no longer sees a monochromatic wave instead a broadband field

Collision Broadening cont'd

How to deal with this?

- Add all the frequencies of jump during collision.
- Use Fourier theory to handle multiple frequencies.
- Assume no collision for time interval T_2 – mean free path

Let

$$d\rho = \rho \omega' d\omega'$$

Be the energy density of the wave in the frequency interval between ω' and $\omega' + d\omega'$

$$dW_{12} = \frac{4\pi}{3\hbar^2 n^2 \epsilon_0} |p_{12}|^2 \rho_{\omega'} \delta(\omega' - \omega_0) d\omega'$$

The overall transition probability is obtained by intergrating over the entire frequency spectrum of the radiation.

We assume the distribution of the values of τ can be described by a probability density

$$P_{\tau} = \frac{1}{T_2} e^{-\tau/T_2}$$

$P_{\tau} d\tau$ is the probability that the time interval between two successive collisions lies between τ and $\tau + d\tau$. T_2 is the mean free path in which there is no collision.

$$\tau_c = \int_0^{\infty} \tau P_{\tau} d\tau = T_2$$

If $P(\tau)$ be the probability that a collision occurs after a time τ , we get

$$P(\tau) = \int_{\tau}^{\infty} P_{\tau} d\tau = \exp(-\tau / \tau_c)$$

The field

$E(\vec{r}, t) = 2E_0 \cos(\omega t)$ is a monochromatic field where $\cos(\omega t)$ gives the phase or the monochromaticity of the field and this field leads to unphysical result

$$W_{12} = \frac{4\pi}{3\hbar^2 n^2 \epsilon_0} |p_{21}|^2 \rho \delta(\Delta\omega)$$

- FOURIER THEORY:

This method is used to handle the multiple frequency

The Fourier theory allows the representation of a function in terms of its frequency or temporal characteristics and one can easily move between the two representation

$$F(t) = \int_{-\infty}^{\infty} F(\omega)e^{-i\omega t} d\omega$$

$$F(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F(t)e^{+i\omega t} dt$$

The power spectrum $W(\omega')$ can be obtained as the Fourier transform of the signal auto-correlation function (Wiener-Kinchine theorem)

CORRELATION:

The method of calculating the similarity of two function is called the correlation integral and result is correlation function.

- **AUTO CORRELATION FUNCTION:**

If the two functions are different, the integral is called cross correlation for same function auto correlation

$$\langle E(t) E(t + \tau) \rangle = \lim_{T \rightarrow \infty} \frac{1}{2T} \int_{-T}^T dt E(t) E(t + \tau)$$

When the functions are aligned we get maximum of Auto -correlation function

$$= \lim_{T \rightarrow \infty} \frac{\pi}{T} \int_{-T}^T dt E(t)^2$$

Power spectrum $W(\omega')$ can be obtained from the Parseval's theorem

$$\int_{-\infty}^{\infty} W(\omega') d\omega' = C \int_{-T}^T E^2(t) dt$$

$$E^2(t) = \int_{-\infty}^{\infty} d\omega d\omega' e^{-i\omega t} e^{-i\omega' t} E(\omega) E(\omega')$$

$$\int_{-\infty}^{\infty} E^2(t) dt = 2\pi \int_{-\infty}^{\infty} d\omega E(\omega) E(-\omega)$$

$$= 2\pi \int_{-\infty}^{\infty} d\omega |E(\omega)|^2$$

$$\rho_{\omega'} = 2\pi \left| E(\omega') \right|^2$$

$$E(\omega') = \frac{1}{2\pi} \int_{t_0}^{t_0+\tau} E_0 e^{-i\omega t + i\omega' t} dt'$$

$$\left| E(\omega') \right|^2 = \frac{2E_0^2}{\pi^2} \left(\frac{\text{Sin}(\omega' - \omega)\tau / 2}{(\omega' - \omega)} \right)^2$$

As $\tau \rightarrow \infty$ Then we again get a δ - function.

Times of flight are distributed according to $P(\tau)$

Total intensity is made up of large number of time segments

$$\rho_{\omega'_{tot}} = \frac{2 |E_0|^2}{T_2 \pi} \int_0^{\infty} e^{-\tau/T_2} \frac{\left(\text{Sin}(\omega' - \omega) \tau / 2 \right)^2}{\left((\omega' - \omega) \right)^2} d\tau$$
$$= \frac{2 |E_0|^2}{T_2 \pi} \left(\frac{1/2}{\left((\omega' - \omega) \right) + \frac{1}{T_2}} \right)$$

$$\rho\omega' = \rho g(\omega' - \omega)$$

where

$$g(\omega' - \omega) = \frac{1}{T_2\pi} \left(\frac{1}{\left((\omega' - \omega)^2 + \frac{1}{T_2^2} \right)} \right)$$

Such that

$$\int_{-\infty}^{\infty} g(\omega' - \omega) d\omega = 1$$

Function is maximum for $\Delta\omega = 0$

Doppler broadening

- This is due to the random motions of the atoms.
- It only occurs in gasses

Consider a field of frequency ω incident on an atom with transition frequency ω_0 which is moving with a velocity v in the propagation direction of the wave. Atom will see a wave of frequency

$$\omega' = \omega \left[1 \pm \frac{V}{C} \right]$$

Due to Doppler effect

- The negative and positive sign applies whether the velocity is in the same or opposite direction to that of the wave. If the atom is moving in the opposite direction to that of wave the frequency observed by the atom is higher than the value observed in lab. frame.

- The absorption will occur only when the apparent frequency ω' as seen from the atom is equal to the atomic transition frequency ω_0

$$\omega' = \omega \left(1 \pm \frac{v}{c} \right) = \omega_0$$

Rewriting above equation

$$\omega = \frac{\omega_0}{\left(1 \pm \frac{v}{c} \right)}$$

This is equivalent to say that atom is not moving but has a resonant frequency equal to

Or
$$\omega_0' = \frac{\omega_0}{\left(1 \pm \frac{v}{c} \right)}$$

Incident field sees a shifted transition frequency of the atom.
Absorption will occur when the frequency ω of e.m.wave is equal to ω_0'

If atom is moving away from the field (same direction)

$$\omega' = \omega \left(1 - \frac{v}{c} \right) = \omega_0$$

$$\Rightarrow \omega = \frac{\omega_0}{\left(1 - \frac{v}{c} \right)}$$

Incident field sees a shifted frequency of the atom and
And absorption occur when this $\omega = \omega_0$ where

$$\omega'_0 = \frac{\omega_0}{\left(1 - \frac{v}{c}\right)}$$

$$\Rightarrow v = (\omega'_0 - \omega_0) \frac{c}{\omega_0}$$

We need to find the spectral function for Doppler broadening

$$g(\Delta\omega) = g(\omega - \omega_0)$$

As atoms are moving with different velocities, therefore field Sees different transition frequencies.

Using kinetic theory of gasses that an atom of mass M in a gas at temperature T has a velocity component between v and $v+ dv$ is given by Maxwellian distribution

$$p_v dv = \left(\frac{M}{2\pi KT} \right)^2 \exp\left(\frac{-Mv^2}{2KT} \right) dv$$

$g(\Delta\omega)d\omega$ gives the probability that the transition frequency lies between ω and $\omega + d\omega$

The frequency function $g(\Delta\omega)$ is related to $p_v dv$

$$g(\omega_0' - \omega_0)d\omega_0' = p_v dv$$

That is the number of atoms absorbing within the frequency interval from ω to $\omega + d\omega$ is equal to the fraction of Atoms moving with velocity between v and $v + dv$ as

$$\left| \frac{dv}{d\omega_0'} \right| = \frac{c}{\omega_0}$$

$$\Rightarrow g(\omega - \omega_0) = \frac{c}{\omega_0} \sqrt{\frac{M}{2\pi KT}} \exp\left[\frac{-Mc^2(\omega - \omega_0)}{2KT\omega_0^2}\right]$$

The shape of curve corresponding to this equation is called Gaussian. The maximum again occurs at $\Delta\omega = 0$

$$g(\Delta\omega)_{\max} = \frac{c}{\omega_0} \left(\frac{M}{2\pi KT}\right)^{1/2}$$

Find FWHM

Spontaneous Emission Rate

SPONTANEOUS EMISSION TRANSITION RATE

$$\left(\frac{dN_2}{dt} \right)_{sp.em} = -AN_2$$

where A is called the Einstein A co-efficient or spontaneous emission transition rate.

- Assume that the material is placed in a blackbody cavity whose walls are kept at a constant temperature T .
- Once thermodynamic equilibrium is reached, an electromagnetic energy density with spectral distribution

$$\rho_{\omega_0} = \frac{\omega_0^2}{\pi^2 c^3} \frac{\hbar \omega_0}{e^{\hbar \omega_0 / kT} - 1} \quad \text{Established}$$

- Material will immersed in this radiation.
- Both stimulated emission and absorption processes will occur in addition to the spontaneous process.
- In thermal equilibrium, number of transitions per second from level 1 to level 2 must be equal to number of transition per second from level 2→1.

$$AN_2^e + W_{21}N_2^e = W_{21}N_1^e$$

Define

$$W_{21} = B_{21} \rho_{\omega_0}$$

and

$$W_{12} = B_{12} \rho_{\omega_0}$$

where B_{21} and B_{12} - called Einstein B co-efficient.
From Boltzmann statistics

$$\frac{N_2^e}{N_1^e} = e^{\left(\frac{-\hbar\omega_0}{kT} \right)}$$

$$\hbar\omega_0 = E_2 - E_1 \quad \text{for} \quad N_2 \rangle N_1$$

$$A \frac{N_2^e}{N_1^e} + B_{21} \rho_{\omega_0} \left(\frac{N_2^e}{N_1^e} \right) = B_{12} \rho_{\omega_0}$$

$$\Rightarrow \rho_{\omega_0} = \frac{A \frac{N_2^e}{N_1^e}}{\left(B_{12} - B_{21} \left(\frac{N_2^e}{N_1^e} \right) \right)}$$

Putting value of $\frac{N_2^e}{N_1^e}$, we get

$$\rho_{\omega_0} = \frac{A e^{-\hbar\omega_0/kT}}{B_{12} - B_{21} e^{-\hbar\omega_0/kT}} = \frac{A}{B_{12} e^{\hbar\omega_0/kT} - B_{21}}$$

For a medium,

$$\rho_{\omega_0} = \frac{\omega_0^2 n^3}{\pi^2 c^3} \frac{\hbar \omega_0}{e^{\hbar\omega_0/kT} - 1}$$

n- refractive index of the medium

Comparing two values we get,

$$\frac{A}{B_{12} e^{-\hbar\omega_0/kT} - B_{21}} = \frac{\omega_0^2 n^3}{\pi^2 c^3} \frac{\hbar\omega_0}{e^{\hbar\omega_0/kT} - 1}$$

$$B_{12} = B_{21} = B$$

Probability of absorption and stimulated emission due to black body radiation are equal.

$$\frac{A/B}{e^{-\hbar\omega_0/kT} - 1} = \frac{\hbar\omega_0^3 n^3}{\pi^2 c^3} \frac{1}{e^{\hbar\omega_0/kT} - 1}$$
$$\Rightarrow \frac{A}{B} = \frac{\hbar\omega_0^3 n^3}{\pi^2 c^3}$$

$$A = \frac{\hbar \omega_0^3 n^3}{\pi^2 c^3} B$$

Once the value of B, due to black body radiation is known
We can find the value of A as we know

$$W = \frac{4\pi}{3n^2 \varepsilon_0 \hbar^2} |p|^2 \rho \delta(\Delta\omega)$$

This is true for monochromatic field.

For black body radiation, the elemental spectral energy density of radiation whose frequency lies between ω and $\omega + d\omega$

$$dW = \frac{4\pi}{3n^2 \varepsilon_0 \hbar^2} |p|^2 \int_0^{\infty} \rho_{\omega} d\omega \delta(\omega - \omega_0)$$

$$dW = \frac{4\pi}{3n^2 \varepsilon_0 \hbar^2} |p|^2 \rho_{\omega_0}$$

$$\Rightarrow B = \frac{4\pi}{3n^2 \varepsilon_0 \hbar^2} |p|^2$$

$$A = \frac{4 \omega_0^3 |p|^2 n}{3 \pi c^3 \epsilon_0 \hbar}$$

This is same result as obtained from Quantum Electrodynamics approach because here we use Planck's law (which is quantum electrodynamically correct). As A increases as the cube of the frequency, so the process of spontaneous emission increases rapidly with frequency. It is easy to produce infrared laser as compared to UV laser. If frequency increases by a factor 10^{10} , then A increases by 10^{30} .

The order of magnitude of spontaneous emission at optical frequency

$$\omega_0 = 10^{15} \text{ hz} \quad \lambda = 5 \times 10^{-5} \text{ cm} \quad |p| = ea$$

where a is Bohr radius $a \approx 10^{-8} \text{ cm}$

Putting these values, we get

$$A = 10^8 \text{ s}^{-1}$$

$$t_{sp} = \frac{1}{A} = 10^{-8} \text{ sec}$$

For magnetic dipole transitions, A is approximately 10^5 times small.

SPECTRUM OF THE SPONTANEOUS EMISSION

Line shape due to natural broadening

- For any transition, the spectrum of the emitted radiation is the same as that observed in absorption
- Assume that an ideal electromagnetic filter-transmitting only those frequencies between ω and $\omega + d\omega$ is placed between the material and the walls of the black body cavity.
- If the material, the filter, and the black body cavity are kept at the same temperature T , then ratio between the populations of the two levels will again be given by

$$\frac{N_2^e}{N_1^e} = e^{\left(-\frac{\hbar \omega_0}{kT} \right)}$$

The density of electromagnetic radiation ρ_ω at any point inside the cavity will also be given by

$$\rho_\omega = \frac{\omega_0^2}{\pi^2 c^3} \frac{\hbar \omega}{e^{\hbar \omega_0 / kT} - 1}$$

and the net exchange of the energy between the material and the cavity within the transmission bandwidth of the filter must be zero.

This means that the energy emitted by the material in the bandwidth $d\omega$ around ω due to spontaneous and stimulated emission must be equal to energy absorbed.

Define a spectral co-efficient A_ω such that

$N_2 A_\omega d\omega$ -Number of atoms per unit time which upon decay emit a photon of frequency between ω and $\omega+d\omega$.

$$A = \int A_\omega d\omega$$

Similarly,

$NB_{\omega}\rho_{\omega}d\omega$ represents the number of transitions per unit absorption or stimulated emission induced by black body radiation with frequency between ω and $\omega+d\omega$.

Equilibrium condition

$$A_{\omega}N_2^e d\omega + B_{\omega}\rho_{\omega}N_2^e d\omega = B_{\omega}\rho_{\omega}N_1^e d\omega$$

Using above equations we get,

$$\frac{A_{\omega}}{B_{\omega}} = \frac{A}{B}$$

where B_ω can be obtained from

$$W = \frac{4\pi}{3n^2 \varepsilon_0 \hbar^2} |p|^2 \rho g_t(\Delta\omega)$$

$$B_\omega = Bg(\Delta\omega)$$

$$\frac{A_\omega}{Bg(\Delta\omega)} = \frac{A}{B} \quad \Rightarrow \quad A_\omega = Ag(\Delta\omega)$$

The spectrum of the radiated wave is the same as for absorption or stimulated emission.

Transition Cross-section

- Transition Cross Section:

For a plane wave the transition rate is proportional to the intensity of e.m. wave.

$$\sigma = \frac{W}{F} = \frac{4\pi}{3\hbar^2} |p|^2 \frac{I}{cn\epsilon_0} \frac{g(\Delta\omega)}{I/\hbar\omega}$$

$$\sigma = \frac{4\pi}{3\hbar^2 cn\epsilon_0} |p|^2 g(\Delta\omega)$$

THANK YOU