GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-14, 06/10/2024)

Unit-3: Semi-classical treatment of radiation-matter interaction

Theoretical basis of interaction of radiation with matter: time dependent perturbation theory, Harmonic perturbation and transition probabilities, Einstein"s A& B co-efficient, LASER and MASER

Time-dependence: time evolution of wavefunction: $i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi$

Schrödinger equation

Hamiltonian Operator, $\hat{H} = -\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right] + \boxed{V(x,y,z,t)}$: valid for any general time-dependent system.

wavefunction, $\Psi = \boxed{\Psi(x,y,z,t)}$; an explicit function of the system's coordinates and time.

For a 1D system, $\Psi \equiv \Psi(x,t)$ and $\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x,t)$

∴ Schrödinger eqn. $-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t) + V(x,t)\Psi(x,t) = i\hbar\frac{\partial \Psi(x,t)}{\partial t}$

Example: $V(x,t) = A\cos(kx-\omega t)$

Special case: V is independent of t; $V(x,t) \rightarrow V(x)$

Approximation: $\Psi(x,t) = \psi(x)\phi(t)$

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x)\phi(t) + V(x)\psi(x)\phi(t) = i\hbar\frac{\partial}{\partial t}\psi(x)\phi(t)$$

or, $\left[-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}\right]\phi(t) + V(x)\psi(x)\phi(t) = i\hbar\left[\frac{d\phi(t)}{dt}\right]\psi(x)$

Dividing throughout by $\psi(x)\phi(t)$, we get

or, $\frac{1}{\psi(x)}\left[-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}\right] + V(x) = \frac{i\hbar}{\phi(t)}\left[\frac{d\phi(t)}{dt}\right]$

$f(x) = g(y)$

$\left.\begin{array}{l} f(x) = K \\ g(y) = K \end{array}\right\}$ K is a constant which is neither a fn. of x nor a fn. of y.

Say the constant is G

∴ $\frac{1}{\psi(x)}\left[-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}\right] + V(x) = G \Rightarrow -\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = G\psi(x)$ —— ①

$\frac{i\hbar}{\phi(t)}\left[\frac{d\phi(t)}{dt}\right] = G \Rightarrow i\hbar\frac{d\phi(t)}{dt} = G\phi(t)$ —— ②

$\frac{d\phi(t)}{\phi(t)} = \frac{G}{i\hbar}dt$

or, $\frac{d\phi(t)}{\phi(t)} = -\frac{iG}{\hbar}dt$

∴ upon integration, $\ln\phi(t) = (-iG/\hbar)t + c$

or, $\phi(t) = e^{-iGt/\hbar}.e^{c}$ or, $\boxed{\phi(t) = Ae^{-iGt/\hbar}}$

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-14, 06/10/2024)

$\phi(t) = Ae^{-iGt/\hbar}$, $i=\sqrt{-1}$ $\quad \frac{iGt}{\hbar}$ must be dimensionless.

$\frac{iG\times\text{time}}{\text{energy}\times\text{time}}$ ⇒ G is a constant which must have the dimension of energy.

$\boxed{G=E}$

$$\therefore\ -\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \Rightarrow \left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right]\psi(x) = E\psi(x)$$

$$\boxed{\hat{H}\psi(x)=E\psi(x)}$$

$$\Psi(x,t) = \psi(x)\,\phi(t)$$
$$= \psi(x)\left[Ae^{-iEt/\hbar}\right]$$

$$\phi(t) = Ae^{-iEt/\hbar}$$

∴ the same argument applies for any two- or three-dimensional system.

$$\Psi(\vec{r},t) = \sum_n \underbrace{a_n(t)}_{\text{explicit functions of time}} u_n(\vec{r})$$

$\hat{H}u_n = E_n u_n$; $\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V$

$\{u_n\}$ → complete orthonormal set of functions

The Sudden approximation: System whose Hamiltonian changes instantaneously from one time-independent form to another time-independent form.

$\hat{H}_1$ at $t \le 0$: u_n are eigenfunctions of $\hat{H}_1$

$\hat{H}_2$ at $t > 0$: v_n " " " $\hat{H}_2$

Assume; system is known to be in one of the eigenstates of $\hat{H}_1$, say u_0, before the change.

$$\Psi(\vec{r},0) = u_0(\vec{r}) = \sum_n a_n(0)\,v_n(\vec{r}) \quad \text{(at times } t>0)$$

$\{u_n\}$, $\{v_n\}$ are complete orthonormal set of eigenfunctions of H_1 and H_2 respectively.

∵ H_2 is time-independent

$$\Psi(\vec{r},t) = \sum_n a_n(0)\,u_n(\vec{r})\,e^{-iE_nt/\hbar}$$

$$\Psi(\vec{r},t) = \sum_n a_n(0)\,v_n(\vec{r})\,e^{-iE_nt/\hbar}$$

E_n = eigenvalues of $\hat{H}_2$

$$\Psi(\vec{r},0) = u_0(\vec{r}) = \sum_n a_n(0)\,v_n(\vec{r})$$

Multiplying both sides by $v_n^*(\vec{r})$ and integrate over all space

$$\langle v_n|u_0\rangle = a_n(0) \Rightarrow a_n(0) = \int v_n^*(\vec{r})\,u_0(\vec{r})\,d\tau$$

$|a_n|^2$: prob. of obtaining any particular value E_n as a result of measurement of the energy of the system.

$$\begin{tikzcd} \underset{(Z=1)}{{}^{3}H} \arrow[r, "\beta"] \arrow[d] & \underset{(Z=2)}{{}^{3}He^{+}} \\ \nu & \end{tikzcd}$$

$${}^{3}H(Z=1): u_{100} = (1/\pi a_0^3)^{1/2} e^{-r/a_0}$$

$${}^{3}He^{+}(Z=2): u_{100} = (8/\pi a_0^3)^{1/2} e^{-2r/a_0}$$

$$\therefore a_n = \int_0^\infty (8/\pi a_0^3)^{1/2} e^{-2r/a_0} (1/\pi a_0^3)^{1/2} e^{-r/a_0}\, 4\pi r^2 dr = (8\sqrt{2}/a_0^3) \int_0^\infty e^{-3r/a_0} r^2 dr$$

$$\text{or, } a_n = 0.838 \Rightarrow |a_n|^2 = 0.70$$ "Entanglement"

Time-Dependence

The basic equation governing the time-evolution of the wave function between measurements is the Schrödinger equation:

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

If the energy eigenfunctions of the system obtained by solving $\hat{H}u_n = E_n u_n$ where, $\hat{H} = (-\hbar^2/2m)\nabla^2 + V$, are u_n then, by completeness, the wave function at any time t can be expressed as a linear combination of u_n

$$\psi(\boldsymbol{r}, t) = \sum_n a_n(t) u_n(\boldsymbol{r})$$

where the coefficients a_n are, in general, functions of time. So far, we have restricted our discussion to systems whose Hamiltonians have no explicit time dependence, but we shall now extend our treatment to include cases where time-varying forces are acting. These problems can often be very difficult to solve and we shall restrict our consideration to those where particular simplifying assumptions can be applied.-

THE SUDDEN APPROXIMATION

This is one of the simplifying assumptions. The sudden approximation can be used when the Hamiltonian changes instantaneously from one time-independent form – say, $\hat{H}_1$ to another – say, $\hat{H}_2$ – at a time which we take to be $t = 0$. This means that,

$$\left.\begin{array}{ll} \hat{H} = \hat{H}_1 & t \le 0 \\ \hat{H} = \hat{H}_2 & t > 0 \end{array}\right\}$$

We assume that the eigenfunctions of $\hat{H}_1$ and $\hat{H}_2$ are u_n and v_n, respectively. We also assume that the system is known to be in one of the eigenstates of $\hat{H}_1$ – say, that is represented by u_0 before the change. We shall obtain the form of the wave function at times $t > 0$, and hence the probabilities that a subsequent energy measurement will yield a particular eigenvalue of $\hat{H}_2$. We first note that the form of the Schrödinger equation ensures that a finite discontinuity in $\hat{H}$ produces a similar discontinuity in $\partial\psi/\partial t$. Therefore ψ must be continuous in time. Thus, immediately before and after the change we must have

$$\Psi(\boldsymbol{r}, 0) = u_0(\boldsymbol{r}) = \sum_n a_n(0) v_n(\boldsymbol{r})$$

where we have used completeness to expand u_0 in terms of the set of eigenfunctions v_n. As $\hat{H}_2$ is time-independent, we can use

$$\Psi(\boldsymbol{r}, t) = \sum_n a_n(0) u_n(\boldsymbol{r}) \exp(-iE_n t/\hbar)$$

to obtain an expression for Ψ at all times greater than zero,

$$\Psi(\boldsymbol{r}, t) = \sum_n a_n(0) v_n(\boldsymbol{r}) \exp(-iE_n t/\hbar)$$

where, the energy levels E_n are the eigenvalues of $\hat{H}_2$. Expressions for the constants $a_n(0)$ can be obtained by multiplying both sides of

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-14, 06/10/2024)

$$\Psi(\boldsymbol{r},0) = u_0(\boldsymbol{r}) = \sum_n a_n(0)v_n(\boldsymbol{r})$$

by v_n^* and integrating over all space. Thus

$$a_n(0) = \int v_n^* u_0 d\tau$$

According to the quantum theory of measurement, the probability of obtaining any particular value E_n as a result of a measurement of the energy at any time after the change is equal to $|a_n|^2$. Following such a measurement, of course, the wave function collapses to become the corresponding eigenfunction v_n. As an example of a practical application of the sudden approximation is the change in the wave function of an atom following a radioactive decay of its nucleus. Tritium (${}^{3}\text{H}$) can decay by the emission of a β particle and a neutrino to become a positively charged, one-electron ion whose nucleus is ${}^{3}\text{He}$. As far as the atomic electron is concerned, therefore, its Hamiltonian has changed suddenly from that corresponding to a hydrogen atom with nuclear charge $Z = 1$ to that of a He^+ ion with $Z = 2$. Using the energy eigenfunctions for a hydrogen-like (one-electron) system, we calculate the probabilities that a subsequent measurement of the energy of the He^+ ion will find it in its ground state. The wave functions of the ground state of the tritium atom and the He^+ ion follow directly from the hydrogenic wave functions

$${}^{3}H: u_{100} = (1/\pi a_0^3)^{1/2}\exp(-r/a_0)$$
$$He^+: u_{100} = (8/\pi a_0^3)^{1/2}\exp(-2r/a_0)$$

The probability of finding the He^+ ion in its ground state is therefore $|A|^2$ where

$$A = \int_0^\infty (8/\pi a_0^3)^{1/2}\exp(-2r/a_0)\,(1/\pi a_0^3)^{1/2}\exp(-r/a_0)\,4\pi r^2 dr$$

$$A = \left(8\sqrt{2}/a_0^3\right)\int_0^\infty \exp(-3r/a_0)\,r^2 dr = 0.838$$

so that the probability, $|A|^2$, is 0.70. A particularly interesting feature of this example follows from the fact that a value of the energy of the He^+ ion can, in principle, be obtained from a knowledge of the energy associated with the nuclear decay, combined with those of the emitted β particle and the neutrino (although in practice the energy of the latter would be very difficult to measure). But the β particle and neutrino could well be a large distance from the atom when these measurements are made, implying that the energy of the ion would have been measured without apparently interfering with it. Nevertheless, quantum mechanics states that this measurement will cause the wave function of the atom to change from a form similar to

$$\Psi(\boldsymbol{r},t) = \sum_n a_n(0)v_n(\boldsymbol{r})\exp\,(-iE_n t/\hbar)$$

to the appropriate energy eigenfunction. This apparent contradiction is an example of *entanglement*.

Time-dependent perturbation theory: a system that evolves in time

Hamiltonian for the system, $H(\vec{r},t)$

Partitioning of the Hamiltonian: $H(\vec{r},t) = H_0(\vec{r}) + V(\vec{r},t)$

$H_0(\vec{r})$ = time-independent unperturbed Hamiltonian

$V(\vec{r},t)$ = time-dependent perturbation

Schrödinger equation: $i\hbar \dfrac{\partial \Psi(\vec{r},t)}{\partial t} = H(\vec{r},t)\,\Psi(\vec{r},t)$

$u_k(\vec{r})$ = eigenfunctions of $H_0(\vec{r})$ $\qquad H_0(\vec{r})\,u_k(\vec{r}) = E_k u_k(\vec{r})$

$\{u_k(\vec{r})\}$: complete orthonormal set $\qquad = \hbar\omega_k u_k(\vec{r})$

$$\langle u_m | u_n \rangle = \delta_{mn} = \begin{cases} 0, & m \neq n \\ 1, & m = n \end{cases}$$

$\Psi(\vec{r},t) = \sum\limits_k c_k(t)\,u_k(\vec{r})\,e^{-iE_k t/\hbar}$: linear combination in terms of a complete orthonormal set of functions.

$$= \sum_k c_k(t)\,u_k(\vec{r}) \exp\left(-\frac{iE_k t}{h/2\pi}\right) = \sum_k c_k(t)\,u_k(\vec{r}) \exp\left(-\frac{ih\nu_k t}{h/2\pi}\right)$$

$$\therefore \Psi(\vec{r},t) = \sum_k c_k(t)\,u_k(\vec{r})\,e^{-i\omega_k t}$$

Schrödinger eqn: $i\hbar \dfrac{\partial \Psi}{\partial t} = H\Psi$

$$\therefore i\hbar \frac{\partial}{\partial t} \sum_k c_k(t)\,u_k(\vec{r})\,e^{-i\omega_k t} = (H_0 + V) \sum_k c_k(t)\,u_k(\vec{r})\,e^{-i\omega_k t}$$

$$\text{or, } i\hbar \sum_k \left[\frac{\partial c_k(t)}{\partial t} u_k(\vec{r})\,e^{-i\omega_k t} + c_k(t)\,u_k(\vec{r}) \frac{\partial}{\partial t} e^{-i\omega_k t}\right] = H_0(\vec{r}) \sum_k c_k(t)\,u_k(\vec{r})\,e^{-i\omega_k t}$$
$$+ V(\vec{r},t) \sum_k c_k(t)\,u_k(\vec{r})\,e^{-i\omega_k t}$$

$$\text{or, } i\hbar \sum_k \left[\frac{dc_k(t)}{dt} - i\omega_k c_k(t)\right] u_k(\vec{r})\,e^{-i\omega_k t} = \sum_k c_k(t)\,\hbar\omega_k u_k(\vec{r})\,e^{-i\omega_k t}$$
$$+ \sum_k c_k(t)\,V(\vec{r},t)\,u_k(\vec{r})\,e^{-i\omega_k t}$$

$$\text{or, } i\hbar \sum_k \frac{dc_k(t)}{dt} u_k(\vec{r})\,e^{-i\omega_k t} + \sum_k c_k(t)\,\cancel{\hbar\omega_k} u_k(\vec{r})\,e^{-i\omega_k t} = \sum_k c_k(t)\,\cancel{\hbar\omega_k} u_k(\vec{r})\,e^{-i\omega_k t}$$
$$+ \sum_k c_k(t)\,V(\vec{r},t)\,u_k(\vec{r})\,e^{-i\omega_k t}$$

or, $$\sum_k \left(i\hbar \frac{dc_k(t)}{dt} - c_k(t)\, V(\vec{r},t) \right) u_k(\vec{r})\, e^{-i\omega_k t} = 0$$

or, $$\sum_k i\hbar \frac{dc_k(t)}{dt} u_k(\vec{r})\, e^{-i\omega_k t} - \sum_k c_k(t)\, V(\vec{r},t)\, u_k(\vec{r})\, e^{-i\omega_k t} = 0$$

Left multiplication by $u_m^*(\vec{r})$

$$\sum_k i\hbar \frac{dc_k(t)}{dt} u_m^*(\vec{r})\, u_k(\vec{r})\, e^{-i\omega_k t} - \sum_k c_k(t)\, u_m^*(\vec{r})\, V(\vec{r},t)\, u_k(\vec{r})\, e^{-i\omega_k t} = 0$$

Integration over all space

$$\sum_k i\hbar \frac{dc_k(t)}{dt} \langle u_m | u_k \rangle e^{-i\omega_k t} - \sum_k c_k(t) \langle u_m | V | u_k \rangle e^{-i\omega_k t} = 0$$

or, $$\sum_k i\hbar \frac{dc_k(t)}{dt} \delta_{mk}\, e^{-i\omega_k t} - \sum_k c_k(t) \langle u_m | V | u_k \rangle e^{-i\omega_k t} = 0$$

For the first term on the LHS to be non-zero, $m=k$, $\delta_{mk}=1$

$$\therefore\ i\hbar \frac{dc_m(t)}{dt} e^{-i\omega_m t} = \sum_k c_k(t) \langle u_m | V | u_k \rangle e^{-i\omega_k t}$$

or, $$\frac{dc_m(t)}{dt} = \frac{1}{i\hbar} \sum_k c_k(t) \langle u_m | V | u_k \rangle e^{i(\omega_m - \omega_k)t}$$

or, $$\frac{dc_m(t)}{dt} = \frac{1}{i\hbar} \sum_k c_k(t)\, V_{mk}\, e^{i\omega_{mk} t}$$ where $V_{mk} = \langle u_m | V | u_k \rangle$, $\omega_{mk} = \omega_m - \omega_k$

$H(\vec{r},t) = H_0(\vec{r}) + \beta V(\vec{r},t)$, β = perturbation parameter, $0 < \beta < 1$

$c_k(t) = c_{k0}(t) + \beta c_{k1}(t) + \beta^2 c_{k2}(t) + \dots$: Taylor series expansion

$$\therefore\ \frac{d}{dt}\left(c_{m0} + \beta c_{m1} + \beta^2 c_{m2} + \dots\right) = \frac{1}{i\hbar} \sum_k \left(c_{k0} + \beta c_{k1} + \beta^2 c_{k2} + \dots\right) \beta V_{mk}\, e^{i\omega_{mk} t}$$

or, $$\frac{dc_{m0}}{dt} + \beta \frac{dc_{m1}}{dt} + \beta^2 \frac{dc_{m2}}{dt} + \dots = \frac{1}{i\hbar} \beta \sum_k c_{k0} V_{mk}\, e^{i\omega_{mk} t} + \frac{1}{i\hbar} \beta^2 \sum_k c_{k1} V_{mk}\, e^{i\omega_{mk} t} + \dots$$

Equating the coefficients of different powers of β

$\frac{dc_{m0}}{dt} = 0$: c_{m0} is a constant of time; an expected result, since the unperturbed Hamiltonian is time-independent.

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-15, 07/10/2024)

$$\frac{dc_{m1}}{dt} = \frac{1}{i\hbar}\sum_k c_{k0} V_{mk} e^{i\omega_{mk}t} \quad \text{or,} \quad c_{m1} = \frac{1}{i\hbar}\sum_k c_{k0}\int_0^t V_{mk} e^{i\omega_{mk}t}\, dt$$

Time-Dependent Perturbation Theory

A very important type of time-dependent problem is one where the Hamiltonian $\hat{H}$ can be written as the sum of a time-independent part $\hat{H}_0$ and a small time-dependent perturbation $\hat{H}'$. An example of this, to which we shall return later, is the case of an atom subject to the oscillating electric field associated with an electromagnetic wave. We shall now describe a method known as time-dependent perturbation theory for obtaining approximate solutions to such problems. We wish to solve the Schrödinger equation,

$$i\hbar\frac{\partial\Psi(\boldsymbol{r},t)}{\partial t} = \hat{H}(\boldsymbol{r},t)\Psi(\boldsymbol{r},t)$$

for the case where, $\hat{H}(\boldsymbol{r},t) = \hat{H}_0(\boldsymbol{r}) + \hat{H}'(\boldsymbol{r},t)$. We assume that the eigenfunctions $u_k(\boldsymbol{r})$ of $\hat{H}_0(\boldsymbol{r})$ are known and expand the wave function $\Psi(\boldsymbol{r},t)$ as a linear combination of these

$$\Psi(\boldsymbol{r},t) = \sum_k c_k(t)u_k(\boldsymbol{r})\exp\left(-iE_kt/\hbar\right)$$

where the expansion coefficients c_k have been defined so as to exclude the factors $\exp\left(-iE_kt/\hbar\right)$, as this simplifies the ensuing argument. Substituting $\hat{H}(\boldsymbol{r},t) = \hat{H}_0(\boldsymbol{r}) + \hat{H}'(\boldsymbol{r},t)$ and $\Psi(\boldsymbol{r},t) = \sum_k c_k(t)u_k(\boldsymbol{r})\exp\left(-iE_kt/\hbar\right)$ in the Schrödinger equation,

$$i\hbar\sum_k\left(\frac{\partial c_k}{\partial t} - i\omega_k c_k\right)u_k\exp(-i\omega_k t) = \sum_k\left[c_k\hbar\omega_k u_k\exp(-i\omega_k t) + c_k\hat{H}'u_k\exp(-i\omega_k t)\right]$$

where, $\omega_k = E_k/\hbar$.

$$\therefore\ \sum_k\left(i\hbar\frac{\partial c_k}{\partial t} - c_k\hat{H}'\right)u_k\exp(-i\omega_k t) = 0$$

We now multiply the above equation by the complex conjugate of one of the unperturbed eigenfunctions, u_m^*, and integrate over all space to get

$$i\hbar\frac{\partial c_m}{\partial t}\exp(-i\omega_m t) - \sum_k c_k\left\langle u_m\middle|\hat{H}'\middle|u_k\right\rangle\exp[i(\omega_m - \omega_k)t] = 0$$

That is,

$$\frac{\partial c_m}{\partial t} = \frac{1}{i\hbar}\sum_k c_k\,\hat{H}'_{mk}\exp(i\omega_{mk}t)$$

where, $\hat{H}'_{mk} = \left\langle u_m\middle|\hat{H}'\middle|u_k\right\rangle$ and $\omega_{mk} = \omega_m - \omega_k$. Everything we have done so far is exact, but we now apply perturbation techniques in a similar manner to that described for the time-independent case. We introduce a constant β, replace $\hat{H}'$ by $\beta\hat{H}'$ and expand the constants c_k in a perturbation series

$$c_k = c_{k0} + \beta c_{k1} + \beta^2 c_{k2} + \cdots$$

Therefore,

$$\frac{\partial c_m}{\partial t} = \frac{1}{i\hbar}\sum_k c_k\,\hat{H}'_{mk}\exp(i\omega_{mk}t)$$

with the use of the above perturbation series becomes,

$$\frac{\partial}{\partial t}(c_{m0} + \beta c_{m1} + \beta^2 c_{m2} + \cdots) = \frac{1}{i\hbar}\sum_k(c_{k0} + \beta c_{k1} + \beta^2 c_{k2} + \cdots)\,\beta\hat{H}'_{mk}\exp(i\omega_{mk}t)$$

$$\text{or,}\ \frac{\partial c_{m0}}{\partial t} + \beta\frac{\partial c_{m1}}{\partial t} + \cdots = \frac{1}{i\hbar}\beta\sum_k c_{k0}\,\hat{H}'_{mk}\exp(i\omega_{mk}t) + \cdots$$

where only the terms having the zeroth and the first powers of β have been retained. Equating the coefficients of the zeroth and the first powers of β we have,

$$\frac{\partial c_{m0}}{\partial t} = 0$$

and

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-15, 07/10/2024)

$$\frac{\partial c_{m1}}{\partial t} = \frac{1}{i\hbar}\sum_k c_{k0}\,\hat{H}'_{mk}\exp(i\omega_{mk}t)$$

Thus, we have, $\partial c_{m0}/\partial t = 0$, with the coefficients c_{m0} are constant in time, which is to be expected as the zero-order Hamiltonian is time independent, and

$$\frac{\partial c_{m1}}{\partial t} = \frac{1}{i\hbar}\sum_k c_{k0}\,\hat{H}'_{mk}\exp(i\omega_{mk}t)\,\text{, where we define } c_{m1} = \frac{1}{i\hbar}\sum_k c_{k0}\int_0^t \hat{H}'_{mk}\exp(i\omega_{mk}t)\,dt$$

We are particularly interested in the case where the system is known to be in a particular eigenstate – say, that represented by u_n – at the time $t = 0$ so that $c_{n0} = 1$, and $c_{k0} = 0,\ k \neq n$.

$$\therefore c_{m1} = \frac{1}{i\hbar}\int_0^t \hat{H}''_{mn}\exp(i\omega_{mn}t)\,dt$$

Time-dependent perturbation theory (Continuation)

$$\frac{dc_{m1}}{dt} = \frac{1}{i\hbar}\sum_k c_{k0} V_{mk} e^{i\omega_{mk}t} \Rightarrow c_{m1} = \frac{1}{i\hbar}\sum_k c_{k0}\int_0^t V_{mk} e^{i\omega_{mk}t} dt$$

Consider the situation where the system is known to be in a particular eigenstate of $\hat{H}_0$, say u_n, at $t=0$.

$$\therefore C_{n0} = 1 \text{ and } C_{k0} = 0, \text{ for } k \neq n$$

$$\therefore C_{m1} = \frac{1}{i\hbar}\int_0^t V'_{mn} e^{i\omega_{mn}t} dt$$

Recall that, $C_{m0} = 0 \, (m \neq n)$; the prob. of finding the system in a state $u_m (m \neq n) = |C_{m1}|^2$, provided C_{m1} is small enough for the perturbation to hold approximately.

We know,

$$\frac{dC_m(t)}{dt} = \frac{1}{i\hbar}\sum_k C_k(t) V_{mk} e^{i\omega_{mk}t} = \frac{1}{i\hbar}\sum_k C_k(t) \exp\left[\frac{i(E_m-E_k)t}{\hbar}\right]\langle u_m|V|u_k\rangle$$

Say, the perturbation, $V(\vec{r},t)$ is applied at $t=0$.

Before the perturbation was applied; stationary state, n, E_n

$\therefore$ At $t=0$, the state is $\Psi(\vec{r},t) = u_n e^{-iE_nt/\hbar}$

The $t=0$ values of the expansion coefficients $C_k(t)$ in $\Psi(\vec{r},t) = \sum_k C_k(t) u_k(\vec{r}) e^{-iE_kt/\hbar}$ are $C_n(0) = 1$ and $C_k(0) = 0$, for $k \neq n$, $C_k(0) = \delta_{kn}$.

} assume: the perturbation $V(\vec{r},t)$ acts only for a very short time. 10^{-15} second

$$\frac{dC_m(t)}{dt} = (i\hbar)^{-1}\sum_k C_k(t) V_{mk} e^{i\omega_{mk}t} = (i\hbar)^{-1}\sum_k C_k(t)\langle u_m|V|u_k\rangle \exp[i(E_m-E_k)t/\hbar]$$

↓ Substitute $C_k(t)$ by the initial values, $C_k(0) = \delta_{kn}$

$$\therefore \frac{dC_m(t)}{dt} \simeq \frac{1}{i\hbar} e^{i\omega_{mn}t} V_{mn} = \frac{1}{i\hbar}\exp[i(E_m-E_n)t/\hbar]\langle u_m|V|u_n\rangle$$

Say, $V(\vec{r},t)$ acts from $t=0$ to $t=t'$

$$\therefore \int_0^{t'} dC_m(t) = \frac{1}{i\hbar}\int_0^{t'} \exp[i(E_m-E_n)t/\hbar]\langle u_m|V|u_n\rangle dt$$

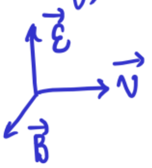
$$C_m(t') - C_m(0) = \frac{1}{i\hbar}\int_0^{t'} \exp[i(E_m-E_n)t/\hbar]\langle u_m|V|u_n\rangle dt$$

$$\text{or, } C_m(t') = \delta_{mn} + \frac{1}{i\hbar}\int_0^{t'} \exp[i(E_m-E_n)t/\hbar]\langle u_m|V|u_n\rangle dt$$

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-16, 14/10/2024)

Interaction of radiation (perturbation) and matter (atom/molecule)

Matter: Quantum mechanically
Radiation (electromagnetic): classically } Spectroscopy (ordinary) is $\boxed{\text{Semi-classical}}$



$\mathcal{E}$ = magnitude of the applied electric field of the electromagnetic radiation

electric force per unit charge

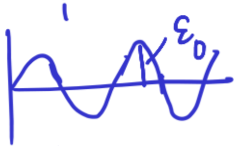
Charge Q_i, $F = Q_i\mathcal{E}_x = -\frac{dV}{dx}$

$\therefore dV = -Q_i\mathcal{E}_x dx$ or, $V = -Q_i\mathcal{E}_x x$

For a system of charges, $V = -\sum_i Q_i x_i \mathcal{E}_x$

This is the time-dependent perturbation for a 1D case, $V(x,t)$

$\mathcal{E}_x = \mathcal{E}_0 \sin(2\pi\nu t - 2\pi z/\lambda)$
$= \mathcal{E}_0 \sin(\omega t - kz)$



ν = freq. of the electric field wave

Neglecting all types of hyperfine interactions

$\therefore V(x,t) = -\mathcal{E}_0 \sum_i Q_i x_i \sin(\omega t - kz_i)$

$\therefore C_m(t') \simeq \delta_{mn} + \frac{1}{i\hbar}\int_0^{t'} \exp(i\omega_{mn}t)\langle u_m|V|u_n\rangle dt$

integral over all space

or, $C_m(t') \simeq \delta_{mn} + \frac{i\mathcal{E}_0}{\hbar}\int_0^{t'} \exp(i\omega_{mn}t)\boxed{\langle u_m|\sum_i Q_i x_i \sin(\omega t - kz_i)|u_n\rangle} dt$

$\sum_i Q_i x_i \sin(\omega t - kz_i)$
$\simeq \sum_i Q_i x_i \sin\omega t$

$kz_i = \frac{2\pi}{\lambda}z_i$ is very small

$2\pi/\lambda$ λ for uv light, ~100 nm

$\omega = 2\pi\nu$ $\omega_{mn} = \frac{E_m - E_n}{\hbar}$

$\frac{e^{i\theta} - e^{-i\theta}}{2i} = \frac{\cancel{\cos\theta} + i\sin\theta - \cancel{\cos\theta} + i\sin\theta}{2i} = \frac{2i\sin\theta}{2i} = \sin\theta \Rightarrow \sin\omega t = (e^{i\omega t} - e^{-i\omega t})/2i$

$\therefore C_m(t') \simeq \delta_{mn} + \frac{i\mathcal{E}_0}{\hbar}\langle u_m|\sum_i Q_i x_i|u_n\rangle \int_0^{t'} e^{i\omega_{mn}t}\frac{e^{i\omega t} - e^{-i\omega t}}{2i} dt$

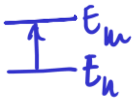
or, $C_m(t') \simeq \delta_{mn} + \frac{\mathcal{E}_0}{2\hbar}\langle u_m|\sum_i Q_i x_i|u_n\rangle \int_0^{t'} \left[e^{i(\omega_{mn}+\omega)t} - e^{i(\omega_{mn}-\omega)t}\right] dt$

or, $C_m(t') \simeq \delta_{mn} + \frac{\mathcal{E}_0}{2\hbar}\langle u_m|\sum_i Q_i x_i|u_n\rangle \left[\frac{e^{i(\omega_{mn}+\omega)t}}{i(\omega_{mn}+\omega)} - \frac{e^{i(\omega_{mn}-\omega)t}}{i(\omega_{mn}-\omega)}\right]_0^{t'}$

$$\therefore c_m(t') \simeq \delta_{mn} + \frac{\varepsilon_0}{2\hbar}\langle u_m|\sum_i Q_i x_i|u_n\rangle \left[\frac{e^{i(\omega_{mn}+\omega)t'}-1}{i(\omega_{mn}+\omega)} - \frac{e^{i(\omega_{mn}-\omega)t'}-1}{i(\omega_{mn}-\omega)}\right]$$

$|c_m(t')|^2$ = prob. of transition to state m from state n.

(a) $\boxed{\omega_{mn} \cong \omega}$, $\frac{e^{i(\omega_{mn}-\omega)t'}-1}{i(\omega_{mn}-\omega)}$ is extremely large $\boxed{\text{l'Hôpital's rule}}$



$$\lim_{(\omega_{mn}-\omega)\to 0} \frac{e^{i(\omega_{mn}-\omega)t'}-1}{i(\omega_{mn}-\omega)} = \lim_{(\omega_{mn}-\omega)\to 0} \frac{it'e^{i(\omega_{mn}-\omega)t'}}{1} = it'$$

absorption of radiation

(b) $\omega_{mn} \simeq -\omega$ stimulated emission

no information about $\boxed{\text{spontaneous emission}}$

$|c_m(t')|^2 \propto |\langle u_m|\sum_i Q_i x_i|u_n\rangle|^2 = |\langle u_m|\mu_x|u_n\rangle|^2$ transition dipole moment integral

$$\hat{\mu} = \hat{i}\sum_i Q_i x_i + \hat{j}\sum_i Q_i y_i + \hat{k}\sum_i Q_i z_i = \hat{i}\mu_x + \hat{j}\mu_y + \hat{k}\mu_z$$

We are particularly interested in the case where the system is known to be in a particular eigenstate – say, that represented by u_n – at the time $t = 0$ so that $c_{n0} = 1$, and $c_{k0} = 0,\ k \neq n$.

$$\therefore c_{m1} = \frac{1}{i\hbar}\int_0^t \hat{H}''_{mn} \exp(i\omega_{mn}t)\, dt$$

Remembering that $c_{m0} = 0\ (m \neq n)$ we see that the probability of finding the system in a state represented by u_m where $m \neq n$ is given by $|c_{m1}|^2$, provided that c_{m1} is small enough for the perturbation approximation to hold.

However, from

$$\frac{dc_m}{dt} = \frac{1}{i\hbar}\sum_k c_k\, \hat{H}'_{mk} \exp(i\omega_{mk}t) = \frac{1}{i\hbar}\sum_k c_k \exp[i(E_m - E_k)\,t/\hbar]\,\langle u_m|\hat{H}'|u_k\rangle$$

one might proceed as follows: Let us suppose that the perturbation $\hat{H}'(\boldsymbol{r},t)$ was applied at time $t = 0$, and that before the perturbation was applied, the system was in the stationary state n with energy E_n. The state at $t = 0$ is hence, $\Psi(\boldsymbol{r},t) = \exp(-iE_nt/\hbar)\,u_n(\boldsymbol{r})$, and the $t = 0$ values of the expansion coefficients in $\Psi(\boldsymbol{r},t) = \sum_k c_k(t)u_k(\boldsymbol{r})\exp(-iE_kt/\hbar)$ are thus $c_n(0) = 1$ and $c_k(0) = 0$, for $k \neq n$: $c_k(0) = \delta_{kn}$. Assume: the perturbation $\hat{H}'(\boldsymbol{r},t)$ acts for only a short time. The change in the expansion coefficients c_k from their initial values at the time the perturbation is applied will be small.

To a good approximation, we can replace the expansion coefficients on the right side of

$$\frac{dc_m}{dt} = \frac{1}{i\hbar}\sum_k c_k\, \hat{H}'_{mk} \exp(i\omega_{mk}t) = \frac{1}{i\hbar}\sum_k c_k \exp[i(E_m - E_k)\,t/\hbar]\,\langle u_m|\hat{H}'|u_k\rangle$$

by their initial values $c_k(0) = \delta_{kn}$.

Therefore, the form

$$\frac{dc_m}{dt} = \frac{1}{i\hbar}\sum_k c_k\, \hat{H}'_{mk} \exp(i\omega_{mk}t) = \frac{1}{i\hbar}\sum_k c_k \exp[i(E_m - E_k)\,t/\hbar]\,\langle u_m|\hat{H}'|u_k\rangle$$

with the coefficients substituted by their initial values $c_k(0) = \delta_{kn}$ become,

$$\frac{dc_m}{dt} \approx \frac{1}{i\hbar}\exp(i\omega_{mn}t)\,\hat{H}'_{mn} = \frac{1}{i\hbar}\exp[i(E_m - E_n)\,t/\hbar]\,\langle u_m|\hat{H}'|u_n\rangle$$

Let the perturbation $\hat{H}'$ act from $t = 0$ to $t = t'$. So, integrating from $t = 0$ to $t = t'$, and using $c_k(0) = \delta_{kn}$

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-16, 14/10/2024)

$$c_m(t') - c_m(0) = \frac{1}{i\hbar}\int_0^{t'} \exp[i(E_m - E_n)\,t/\hbar]\,\langle u_m|\hat{H}'|u_n\rangle\,dt$$

which becomes

$$c_m(t') = \delta_{mn} + \frac{1}{i\hbar}\int_0^{t'} \exp[i(E_m - E_n)\,t/\hbar]\,\langle u_m|\hat{H}'|u_n\rangle\,dt$$

Use of the above approximate result for the expansion coefficients in

$$\Psi(\boldsymbol{r},t) = \sum_k c_k(t)u_k(\boldsymbol{r})\exp(-iE_k t/\hbar)$$

gives the desired approximation to the state function at time t' for the case that the time-dependent perturbation $\hat{H}'$ is applied at $t = 0$ to a system in stationary state n. For times after t', the perturbation has ceased to act, and $\hat{H}' = 0$. Therefore,

$$\frac{dc_m}{dt} = \frac{1}{i\hbar}\sum_k c_k\,\hat{H}'_{mk}\exp(i\omega_{mk}t) = \frac{1}{i\hbar}\sum_k c_k\exp[i(E_m - E_k)\,t/\hbar]\,\langle u_m|\hat{H}'|u_k\rangle$$

gives $dc_m/dt = 0$ for $t > t'$, so $c_m(t) = c_m(t')$ for $t \geq t'$. Therefore, for times after exposure to the perturbation, the state function is

$$\Psi(\boldsymbol{r},t) = \sum_m c_m(t')u_m(\boldsymbol{r})\exp(-iE_m t/\hbar)\ \text{for}\ t \geq t'$$

where $c_m(t')$ is given by

$$c_m(t') = \delta_{mn} + \frac{1}{i\hbar}\int_0^{t'} \exp[i(E_m - E_n)\,t/\hbar]\,\langle u_m|\hat{H}'|u_n\rangle\,dt.$$

Note that, in the above expression for

$$\Psi(\boldsymbol{r},t) = \sum_m c_m(t')u_m(\boldsymbol{r})\exp(-iE_m t/\hbar)\ \text{for}\ t \geq t'$$

$\Psi(\boldsymbol{r},t)$ is a superposition of the eigenfunctions $u_m(\boldsymbol{r})$ of the energy operator $\hat{H}_0(\boldsymbol{r})$, the expansion coefficients being $c_m(t')\exp(-iE_m t/\hbar)$. A measurement of the system's energy at a time after t' will give one of the eigenvalues E_m of the operator $\hat{H}_0(\boldsymbol{r})$, and the probability of getting E_m equals the square of the absolute value of the expansion coefficient that multiplies $u_m(\boldsymbol{r})$.

A measurement of the system's energy at a time after t' will give one of the eigenvalues E_m of the operator $\hat{H}_0(\boldsymbol{r})$, and the probability of getting E_m equals the square of the absolute value of the expansion coefficient that multiplies $u_m(\boldsymbol{r})$. Therefore, this probability becomes,

$$|c_m(t')\exp(-iE_m t/\hbar)|^2 = |c_m(t')|^2.$$

The time-dependent perturbation changes the system's state function from

$$\Psi(\boldsymbol{r},t) = u_n(\boldsymbol{r})\exp(-iE_n t/\hbar)$$

to the superposition

$$\Psi(\boldsymbol{r},t) = \sum_m c_m(t')u_m(\boldsymbol{r})\exp(-iE_m t/\hbar)\ \text{for}\ t \geq t'.$$

Measurement of the energy then changes $\Psi(\boldsymbol{r},t)$ to one of the energy-eigenfunctions $u_m(\boldsymbol{r})\exp(-iE_m t/\hbar)$. The net result is a transition from stationary state n to stationary state m, the probability of such a transition being $|c_m(t')|^2$.

4. Interaction of Radiation and Matter: Towards Spectroscopy

We now consider the interaction of an atom/molecule with electromagnetic radiation. A proper quantum-mechanical approach would treat both the atom and the radiation quantum mechanically, but we shall simplify things by using the classical picture of the light as an electromagnetic wave of oscillating electric and magnetic fields. Thus, traditional spectroscopy is semi-classical. Usually, the interaction between the radiation's magnetic field and the atom's/molecule's charges is much weaker than the interaction between

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-16, 14/10/2024)

the radiation's electric field and the charges, so we shall consider only the latter interaction. Say, $\mathcal{E}$ is the electric field (the magnitude, or the scalar part only of the actual field, $\vec{\mathcal{E}}$) associated with the electromagnetic radiation ⇒ a plane-polarized radiation. The electric field is defined as the force per unit charge, so the force on charge Q_i is $F = Q_i\mathcal{E}_x = -dV/dx$. Integration leads to: $V = -Q_i\mathcal{E}_x x$, potential energy of interaction between the radiation's electric field and the charge (where the integration constant has been scaled to zero). For a system that has several charges, $V = -\sum_i Q_i\, x_i\mathcal{E}_x$. This potential energy of interaction between the radiation's electric field and several charges $V = -\sum_i Q_i\, x_i\mathcal{E}_x$ is the time-dependent perturbation, $\hat{H}'(t)$. The space and time dependence of the electric field of an electromagnetic wave traveling in the z direction with wavelength λ and frequency ν is given by $\mathcal{E}_x = \mathcal{E}_0 \sin(2\pi\nu t - 2\pi z/\lambda)$, where $\mathcal{E}_0$ (the amplitude) is the maximum value of $\mathcal{E}_x$.

$$\therefore \hat{H}'(t) = -\mathcal{E}_0 \sum_i Q_i\, x_i \sin(2\pi\nu t - 2\pi z_i/\lambda)$$

The summation in the above expression runs over all the electrons and nuclei of the atom or molecule.

We define: $\omega = 2\pi\nu$, the angular/circular frequency, $k = 2\pi/\lambda$, the wave number, and $\omega_{mn} = (E_m - E_n)/\hbar$.

$$\therefore \hat{H}'(t) = -\mathcal{E}_0 \sum_i Q_i\, x_i \sin(\omega t - kz_i)$$

We recall that,

$$c_m(t') \approx \delta_{mn} + \frac{1}{i\hbar}\int_0^{t'} \exp[i(E_m - E_n)\,t/\hbar]\,\langle u_m|\hat{H}'|u_n\rangle\, dt$$

Therefore, from

$$\hat{H}'(t) = -\mathcal{E}_0 \sum_i Q_i\, x_i \sin(\omega t - kz_i)$$

and,

$$c_m(t') \approx \delta_{mn} + \frac{1}{i\hbar}\int_0^{t'} \exp(i\omega_{mn}t)\,\langle u_m|\hat{H}'|u_n\rangle\, dt$$

we write,

$$c_m(t') \approx \delta_{mn} + \frac{i\mathcal{E}_0}{\hbar}\int_0^{t'} \exp(i\omega_{mn}t)\,\langle u_m|\textstyle\sum_i Q_i\, x_i \sin(\omega t - kz_i)\,|u_n\rangle dt$$

Note that, the integral $\langle u_m|\sum_i Q_i\, x_i \sin(\omega t - kz_i)\,|u_n\rangle$ is over all space, but significant contributions to its magnitude come only from regions where u_m and u_n are of significant magnitude. In regions well outside the atom/molecule, u_m and u_n are vanishingly small, and such regions can be ignored. Let the origin of the coordinate system be chosen within the atom/molecule. Since regions well outside the atom can be ignored, the coordinate z_i can be considered to have a maximum magnitude of the order of one nm. For ultraviolet light, the wavelength λ is on the order of 10^2 nm. For visible, infrared, microwave, and radiofrequency radiation, λ is even larger.

$\therefore kz_i = 2\pi z_i/\lambda$ is very small and can be neglected.

$$\therefore \sum_i Q_i\, x_i \sin(\omega t - kz_i) \cong \sum_i Q_i\, x_i \sin\omega t$$

Now, note that, since,

$$\frac{e^{i\theta} - e^{-i\theta}}{2i} = \frac{\cos\theta + i\sin\theta - [\cos(-\theta) + i\sin(-\theta)]}{2i} = \frac{\cos\theta + i\sin\theta - (\cos\theta - i\sin\theta)}{2i} = \sin\theta$$

hence, $\sin\omega t = \left(e^{i\omega t} - e^{-i\omega t}\right)/2i$. Therefore,

$$c_m(t') \approx \delta_{mn} + \frac{i\mathcal{E}_0}{\hbar}\int_0^{t'} \exp(i\omega_{mn}t)\,\langle u_m|\textstyle\sum_i Q_i\, x_i \sin(\omega t - kz_i)\,|u_n\rangle dt$$

becomes,

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-16, 14/10/2024)

$$c_m(t') \approx \delta_{mn} + \frac{\mathcal{E}_0}{2\hbar}\langle u_m | \textstyle\sum_i Q_i\, x_i | u_n\rangle \displaystyle\int_0^{t'} \left[e^{i(\omega_{mn}+\omega)t} - e^{i(\omega_{mn}-\omega)t}\right] dt$$

We note that,

$$\int_0^{t'} e^{at}\, dt = \frac{1}{a}\left(e^{at'} - 1\right),$$

and using this result, we get,

$$c_m(t') \approx \delta_{mn} + \frac{\mathcal{E}_0}{2\hbar}\langle u_m | \textstyle\sum_i Q_i\, x_i | u_n\rangle \displaystyle\left[\frac{e^{i(\omega_{mn}+\omega)t'} - 1}{i(\omega_{mn}+\omega)} - \frac{e^{i(\omega_{mn}-\omega)t'} - 1}{i(\omega_{mn}-\omega)}\right]$$

For $m \neq n$, $\delta_{mn} = 0$. We know, $|c_m(t')|^2$ gives the probability of a transition to state m from state n. There are two cases where this probability becomes of significant magnitude. We now explore these two cases in details.

Case 1: $\boldsymbol{\omega_{mn} = \omega}$

If $\omega_{mn} = \omega$, the denominator of the second fraction in brackets is zero and this fraction's absolute value is large, but not infinite. This is so because of the l'Hôpital's rule:

$$\lim_{(\omega_{mn}-\omega)\to 0} \frac{e^{i(\omega_{mn}-\omega)t'} - 1}{i(\omega_{mn}-\omega)} = \lim_{(\omega_{mn}-\omega)\to 0} it' e^{i(\omega_{mn}-\omega)t'}/1 = it'$$

For $\omega_{mn} = \omega$, [recall, $\omega = 2\pi\nu$, and $\omega_{mn} = (E_m - E_n)/\hbar$], $E_m - E_n = h\nu$. Exposure of the atom/molecule to radiation of frequency ν has produced a transition from stationary state n to stationary state m, where (since ν is positive) $E_m > E_n$. We might suppose that the energy for this transition came from the system's absorption of a photon of energy $h\nu$. This supposition is confirmed by a fully quantum-mechanical treatment (called **quantum field theory**) in which the radiation is treated quantum mechanically rather than classically. We have absorption of radiation with a consequent increase in the system's energy.

Case 2: $\boldsymbol{\omega_{mn} = -\omega}$

For $\omega_{mn} = -\omega$, we get $E_n - E_m = h\nu$. Exposure to radiation of frequency ν has induced a transition from stationary state n to stationary state m, where (since ν is positive) $E_n > E_m$. The system has gone to a lower energy level, and a quantum field theory treatment shows that a photon of energy $h\nu$ is emitted in this process. This is stimulated emission of radiation. Stimulated emission occurs in lasers.

There is a **defect** in our treatment → it does not predict spontaneous emission.

Spontaneous emission: the emission of a photon by a system not exposed to radiation, the system falling to a lower energy level in the process. Quantum field theory does predict spontaneous emission. Note that, from

$$c_m(t') \approx \delta_{mn} + \frac{\mathcal{E}_0}{2i\hbar}\langle u_m | \textstyle\sum_i Q_i\, x_i | u_n\rangle \displaystyle\left[\frac{e^{i(\omega_{mn}+\omega)t'} - 1}{i(\omega_{mn}+\omega)} - \frac{e^{i(\omega_{mn}-\omega)t'} - 1}{i(\omega_{mn}-\omega)}\right]$$

we can say that, that the probability of absorption, $|c_m(t')|^2$, is proportional to $|\langle u_m | \sum_i Q_i\, x_i | u_n\rangle|^2$.

The quantity, $\sum_i Q_i\, x_i$ is the x component of the system's electric dipole moment operator, $\hat{\boldsymbol{\mu}}$, which is given by

$$\hat{\boldsymbol{\mu}} = \boldsymbol{i}\sum_i Q_i\, x_i + \boldsymbol{j}\sum_i Q_i\, y_i + \boldsymbol{k}\sum_i Q_i\, z_i = \boldsymbol{i}\hat{\mu}_x + \boldsymbol{j}\hat{\mu}_y + \boldsymbol{k}\hat{\mu}_z$$

$\boldsymbol{i}, \boldsymbol{j}, \boldsymbol{k}$ are unit vectors along the axes and $\hat{\mu}_x, \hat{\mu}_y, \hat{\mu}_z$ are the components of $\hat{\boldsymbol{\mu}}$. We assumed polarized radiation with an electric field in the x direction only. If the radiation has electric-field components in the y and z directions also, then the probability of absorption will be proportional to

$$|\langle u_m | \hat{\mu}_x | u_n\rangle|^2 + \left|\langle u_m | \hat{\mu}_y | u_n\rangle\right|^2 + |\langle u_m | \hat{\mu}_z | u_n\rangle|^2 = |\langle u_m | \hat{\boldsymbol{\mu}} | u_n\rangle|^2$$

The above relation holds true since

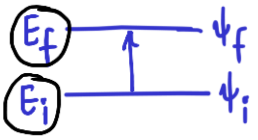
$$|\boldsymbol{A}| = \left(A_x^2 + A_y^2 + A_z^2\right)^{1/2}$$

for a vector $\boldsymbol{A}$. The integral, $\langle u_m|\hat{\boldsymbol{\mu}}|u_n\rangle = \boldsymbol{\mu_{mn}}$ is called the **transition (dipole) moment** (integral). When $\boldsymbol{\mu_{mn}} = 0$, the transition between states m and n with absorption or emission of radiation is said to be forbidden. Allowed transitions have $\boldsymbol{\mu_{mn}} \neq 0$. Because of approximations made in the derivation of

$$c_m(t') \approx \delta_{mn} + \frac{\mathcal{E}_0}{2i\hbar}\langle u_m|\sum_i Q_i\, x_i|u_n\rangle\left[\frac{e^{i(\omega_{mn}+\omega)t'}-1}{i(\omega_{mn}+\omega)} - \frac{e^{i(\omega_{mn}-\omega)t'}-1}{i(\omega_{mn}-\omega)}\right]$$

forbidden transitions may have some small probability of occurring.

Application to a two-level system



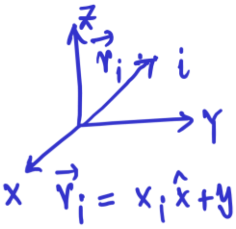
ψ_i, ψ_f : stationary states ; $\boxed{\psi_n(\vec{r},t) = \phi_n(\vec{r})\, e^{-iE_nt/\hbar}}$

$V(\vec{r})$

$i\hbar\dfrac{\partial\psi}{\partial t} = \hat{H}_0\psi$; $\hat{H}_0\phi_n(\vec{r}) = E_n\phi_n(\vec{r})$

$\psi_n^*(\vec{r},t)\psi_n(\vec{r},t) = \phi_n^*(\vec{r})\, \underline{e}^{iE_nt/\hbar}\, \phi_n(\vec{r})\, \underline{e}^{-iE_nt/\hbar} = \phi_n^*(\vec{r})\,\phi_n(\vec{r})$

$\Rightarrow |\psi_n(\vec{r},t)|^2 = |\phi_n(\vec{r})|^2$



$\vec{r}_i = x_i\hat{x} + y_i\hat{y} + z_i\hat{z}$

q_i = point charge at i

dipole moment operator, $\hat{\vec{\mu}} = \sum_i q_i\hat{\vec{r}}_i$ $\quad$ $\hat{\vec{r}}_i$ = position operator at i

$\mu_x = \sum_i q_i x_i$, $\mu_y = \sum_i q_i y_i$, $\mu_z = \sum_i q_i z_i$

$\hat{\vec{\mu}}_{if} = \langle \psi_i(\vec{r},t) | \hat{\vec{\mu}} | \psi_f(\vec{r},t) \rangle$; intensity $\propto |\hat{\vec{\mu}}_{if}|^2$

Assume: an isolated molecule (no intermolecular interaction); kept in the dark
(no interaction with radiation, time-independent)

$\hat{H}_0$: Hamiltonian of the isolated molecule; time-independent

$i\hbar\dfrac{\partial\psi}{\partial t} = \hat{H}_0\psi \rightarrow$ solutions give stationary states.
$\psi_n(\vec{r},t) = \phi_n(\vec{r})\, e^{-iE_nt/\hbar}$

$\hat{H}_0\phi_n(\vec{r}) = E_n\phi_n(\vec{r})$; $\psi_n^*(\vec{r},t)\psi_n(\vec{r},t) = \phi_n^*(\vec{r})\, e^{iE_nt/\hbar}\,\phi_n(\vec{r})\, e^{-iE_nt/\hbar} = \phi_n^*(\vec{r})\,\phi_n(\vec{r})$

$|\psi_n(\vec{r},t)|^2 = |\phi_n(\vec{r})|^2$

optical range : UV ($\lambda \sim 10^3$ Å) to IR ($\lambda \sim 10^7$ Å)

a molecule has a typical dimension of a few Å

light is constant in every part of the molecule

for a monochromatic light of freq. ν, $\vec{\mathcal{E}} = \mathcal{E}_0\cos(2\pi\nu t) = \mathcal{E}_0\cos\omega t$

$f(\vec{r},t)$ = electrical potential at a point $\vec{r}$ of the electric field $= -\vec{r}\cdot\vec{\mathcal{E}}$ (scalar pdt.)

$V(\vec{r},t)$ = potential energy of interaction of a point charge q in the field
$= q\,f(\vec{r},t)$

$\therefore$ For a system of charges, $V(\vec{r},t) = \sum_i q_i f_i(\vec{r}_i,t) = \sum_i q_i(-\vec{r}_i\cdot\vec{\mathcal{E}}) = -\sum_i q_i\vec{r}_i\cdot\vec{\mathcal{E}}_0\cos\omega t$

or, $V(\vec{r},t) = -\sum_i \vec{\mu}_i\cdot\vec{\mathcal{E}}$ $\qquad$ $\boxed{V(\vec{r},t) = -\vec{\mu}\cdot\vec{\mathcal{E}}}$

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-17, 15/10/2024)

Say, the light source is switched on at $t=0$

Overall Hamiltonian, $\hat{H} = \hat{H}_0 + \underline{V(\vec{r},t)}$ at $t \geq 0$

$V(\vec{r},t)$: acts as a small perturbation applied for a short span of time

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

$$\psi_n(\vec{r},t) = \phi_n(\vec{r})\, e^{-iE_n t/\hbar}$$

$$\hat{H}_0 \phi_n(\vec{r}) = E_n \phi_n(\vec{r})$$

$\{\phi_n(\vec{r})\}$: complete orthonormal set of functions. $\Rightarrow \langle \phi_m | \phi_n \rangle = \delta_{mn}$

$$\begin{tikzcd} & \{\phi_n(\vec{r})\} \arrow[dl] \arrow[dr] & \\ \psi_1(\vec{r},t) & & \psi_2(\vec{r},t) \end{tikzcd}$$

$$\left.\begin{aligned} \psi_1(\vec{r},t) &= \phi_1(\vec{r})\, e^{-iE_1 t/\hbar} \\ \psi_2(\vec{r},t) &= \phi_2(\vec{r})\, e^{-iE_2 t/\hbar} \end{aligned}\right\}$$

$\phi_1(\vec{r})$, $\phi_2(\vec{r})$ are eigenfunctions of $\hat{H}_0$ with eigenvalues E_1 and E_2.

$$i\hbar \frac{\partial \psi_1}{\partial t} = \hat{H}_0 \psi_1$$

$$\text{LHS} = i\hbar\, \phi_1(\vec{r})\, e^{-iE_1 t/\hbar}\left(-\frac{iE_1}{\hbar}\right) = E_1\, \phi_1(\vec{r})\, e^{-iE_1 t/\hbar}$$

$$\text{RHS} = \hat{H}_0\, \phi_1(\vec{r})\, e^{-iE_1 t/\hbar} = E_1\, \phi_1(\vec{r})\, e^{-iE_1 t/\hbar}$$

$\therefore$ LHS = RHS

Say, at $t \geq 0$

$$\psi(\vec{r},t) = a_1(t)\, \psi_1(\vec{r},t) + a_2(t)\, \psi_2(\vec{r},t)$$

$|a_1(t)|^2$ = prob. of finding the system in state 1

$|a_2(t)|^2$ = " " " " " " 2

$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi$, $\hat{H} = \hat{H}_0 + V(\vec{r},t)$, $V(\vec{r},t) = -\vec{\mu}\cdot\vec{\mathcal{E}}$

or, $i\hbar \frac{\partial}{\partial t}\left[a_1(t)\,\psi_1(\vec{r},t) + a_2(t)\,\psi_2(\vec{r},t)\right] = \left[\hat{H}_0 + V(\vec{r},t)\right]\left[a_1(t)\,\psi_1(\vec{r},t) + a_2(t)\,\psi_2(\vec{r},t)\right]$

or, $i\hbar\left[\frac{da_1}{dt}\psi_1 + a_1\frac{\partial \psi_1}{\partial t} + \frac{da_2}{dt}\psi_2 + a_2\frac{\partial \psi_2}{\partial t}\right] = a_1\hat{H}_0\psi_1 + Va_1\psi_1 + a_2H_0\psi_2 + Va_2\psi_2$

$$i\hbar\frac{\partial \psi_1}{\partial t} = H_0\psi_1 \qquad i\hbar\frac{\partial \psi_2}{\partial t} = H_0\psi_2$$

$$a_1 i\hbar\frac{\partial \psi_1}{\partial t} = a_1H_0\psi_1 \qquad a_2 i\hbar\frac{\partial \psi_2}{\partial t} = a_2H_0\psi_2$$

or, $i\hbar\frac{da_1}{dt}\psi_1 + \underbrace{\cancel{a_1 i\hbar\frac{\partial \psi_1}{\partial t}}}_{\cancel{a_1H_0\psi_1}} + i\hbar\frac{da_2}{dt}\psi_2 + \underbrace{\cancel{a_2 i\hbar\frac{\partial \psi_2}{\partial t}}}_{\cancel{a_2H_0\psi_2}} = \cancel{a_1\hat{H}_0\psi_1} + Va_1\psi_1 + \cancel{a_2H_0\psi_2} + Va_2\psi_2$

or, $i\hbar\frac{da_1}{dt}\psi_1 + i\hbar\frac{da_2}{dt}\psi_2 = Va_1\psi_1 + Va_2\psi_2$ or, $i\hbar\left[\frac{da_1}{dt}\psi_1 + \frac{da_2}{dt}\psi_2\right] = Va_1\psi_1 + Va_2\psi_2$

Left multiplication with $\phi_2^*(\vec{r})$ and integration over all space.

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-17, 15/10/2024)

$$i\hbar\left[\frac{da_1}{dt}\psi_1 + \frac{da_2}{dt}\psi_2\right] = Va_1\psi_1 + Va_2\psi_2$$

$$\text{or, } i\hbar\frac{da_1}{dt}\int\phi_2^*\psi_1\,dv + i\hbar\frac{da_2}{dt}\int\phi_2^*\psi_2\,dv = a_1\int\phi_2^*V\psi_1\,dv + a_2\int\phi_2^*V\psi_2\,dv$$

$$\text{or, } i\hbar\frac{da_1}{dt}\int\phi_2^*\phi_1e^{-iE_1t/\hbar}dv + i\hbar\frac{da_2}{dt}\int\phi_2^*\phi_2e^{-iE_2t/\hbar}dv = a_1\int\phi_2^*V\phi_1e^{-iE_1t/\hbar}dv + a_2\int\phi_2^*V\phi_2e^{-iE_2t/\hbar}dv$$

$$\text{or, } i\hbar\frac{da_1}{dt}e^{-iE_1t/\hbar}\underbrace{\langle\phi_2|\phi_1\rangle}_{=0} + i\hbar\frac{da_2}{dt}e^{-iE_2t/\hbar}\underbrace{\langle\phi_2|\phi_2\rangle}_{=1} = a_1e^{-iE_1t/\hbar}\langle\phi_2|V|\phi_1\rangle + a_2e^{-iE_2t/\hbar}\langle\phi_2|V|\phi_2\rangle$$

$$\text{or, } i\hbar\frac{da_2}{dt}e^{-iE_2t/\hbar} = a_1e^{-iE_1t/\hbar}\langle\phi_2|V|\phi_1\rangle + a_2e^{-iE_2t/\hbar}\langle\phi_2|V|\phi_2\rangle$$

$$\text{or, } i\hbar\frac{da_2}{dt} = a_1e^{i(E_2-E_1)t/\hbar}\langle\phi_2|V|\phi_1\rangle + a_2\langle\phi_2|V|\phi_2\rangle$$

Application to a two-level system

Let us think of an atom/molecule, which, for simplicity, we will treat as a two-level system to maintain a simplicity of our formal treatment. The system is initially isolated (no interatomic/intermolecular interactions), and is kept in the dark (no interaction with light/electromagnetic waves). Such an initial state of the system is defined well by the zeroth-order/unperturbed Hamiltonian $\hat{H}_0$ and satisfies the Schrödinger equation

$$i\hbar\frac{\partial\psi}{\partial t} = \hat{H}_0\psi \tag{1}$$

The solutions of the above equation are the stationary states

$$\psi_n(\vec{r},t) = \phi_n(\vec{r})e^{-iE_nt/\hbar}$$

such that, $\hat{H}_0\phi_n(\vec{r}) = E_n\phi_n(\vec{r})$, with the property that

$$\psi_n^*(\vec{r},t)\psi_n(\vec{r},t) = \phi_n^*(\vec{r})e^{iE_nt/\hbar}\phi_n(\vec{r})e^{-iE_nt/\hbar} = \phi_n^*(\vec{r})\phi_n(\vec{r}) \Rightarrow |\psi_n(\vec{r},t)|^2 = |\phi_n(\vec{r})|^2$$

Now let us consider the interaction of this system with light/electromagnetic radiation (of optical range, UV to IR, with the wavelength spanning from $\sim 10^3$ Å to $\sim 10^7$ Å), having an electric field $\vec{\mathcal{E}}$ and a magnetic field $\vec{B}$. Since the interaction of the atomic/molecular electrons with $\vec{\mathcal{E}}$ is much stronger than all other interactions, we take into consideration this interaction only, and treat all others as hyperfine interactions. A typical molecule has a dimension of a few Å. Hence, for all practical purposes, light is assumed to be homogeneous in every part of the molecule. For a monochromatic light of frequency ν,

$$\vec{\mathcal{E}} = \vec{\mathcal{E}}_0\cos(2\pi\nu t) = \vec{\mathcal{E}}_0\cos\omega t$$

The electrons of the atom/molecule interact with $\vec{\mathcal{E}}$ of light along the direction of $\vec{\mathcal{E}}$. Say, $f(\vec{r},t)$ is the electrical potential of the electric field at a point $\vec{r}$ in space. Hence, $f(\vec{r},t)$ is given by the scalar product

$$f(\vec{r},t) = -\vec{r}\cdot\vec{\mathcal{E}}$$

If $V(\vec{r},t)$ is the potential energy of interaction of a point charge q with the electric field $\vec{\mathcal{E}}$, then

$$V(\vec{r},t) = qf(\vec{r},t)$$

However, our system is essentially a system of such point charges (electrons), and

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-17, 15/10/2024)

$$V(\vec{r},t)=\sum_i q_i\,f_i(\vec{r},t)=\sum_i q_i\left(-\vec{r}\cdot\vec{\mathcal{E}}\right)=-\sum_i q_i\,\vec{r}_i\cdot\vec{\mathcal{E}}=-\sum_i \vec{\mu}_i\cdot\vec{\mathcal{E}}$$

Hence, for our treatment, the light source acts as the perturbation, and the corresponding perturbation potential has the form $\hat{V}(\vec{r},t)=-\vec{\mu}\cdot\vec{\mathcal{E}}$. We assume that we switch on the light source (perturbation) at $t=0$, and that $\hat{V}(\vec{r},t)$ acts as a small perturbation, so that the time-dependent perturbation theory is applicable. Therefore, at all times $t\geq 0$, the Hamiltonian for the system becomes

$$\hat{H}=\hat{H}_0+\hat{V}(\vec{r},t)\text{ at }t\geq 0$$

We also recall that; the unperturbed system is defined by (1) in a manner such that $\hat{H}_0\phi_n(\vec{r})=E_n\phi_n(\vec{r})$ and the stationary states are given by $\psi_n(\vec{r},t)=\phi_n(\vec{r})e^{-iE_nt/\hbar}$. Our system has an infinite number of stationary states, and $\{\phi_n(\vec{r})\}$ spans a complete orthonormal set of functions. To preserve the simplicity of our derivation, we assume that our molecule has only two stationary states, $\psi_1(\vec{r},t)$ and $\psi_2(\vec{r},t)$, such that,

$$\psi_1(\vec{r},t)=\phi_1(\vec{r})e^{-iE_1t/\hbar},\psi_2(\vec{r},t)=\phi_2(\vec{r})e^{-iE_2t/\hbar}$$

$\phi_1(\vec{r})$ and $\phi_2(\vec{r})$ are the eigenfunctions of $\hat{H}_0$. We solve

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

Does the Schrödinger equation get satisfied with $\hat{H}_0$ and the above forms of $\psi_1(\vec{r},t)$ and $\psi_2(\vec{r},t)$?

Let us check with $\psi_1(\vec{r},t)$, where $\psi_1(\vec{r},t)=\phi_1(\vec{r})e^{-iE_1t/\hbar}$. Hence,

$$i\hbar\frac{\partial}{\partial t}\phi_1(\vec{r})e^{-iE_1t/\hbar}=\hat{H}_0\phi_1(\vec{r})e^{-iE_1t/\hbar}$$

$$\therefore \text{LHS}=i\hbar\phi_1(\vec{r})e^{-iE_1t/\hbar}\left(-\frac{iE_1}{\hbar}\right)=E_1\phi_1(\vec{r})e^{-iE_1t/\hbar}\text{ and RHS}=E_1\phi_1(\vec{r})e^{-iE_1t/\hbar}$$

$$\Rightarrow \text{LHS}=\text{RHS}$$

One may verify with $\phi_2(\vec{r})$ in the same manner.

Say, the system is initially (at $t=0$) in state ψ_1. Hence, the initial state wavefunction for the system is given by $\psi_1(\vec{r},t)$. At $t=0$, the light source is switched on. For any time $t\geq 0$, $\psi_1(\vec{r},t)$ is not an eigenfunction of $\hat{H}$. Say, at $t\geq 0$, the wavefunction has the form

$$\psi(\vec{r},t)=a_1(t)\psi_1(\vec{r},t)+a_2(t)\psi_2(\vec{r},t)\tag{2}$$

where a_1 and a_2 are the combining coefficients and are functions of t only, while ψ_1, ψ_2 and $\hat{V}$ are functions of both space and time. We note that, any $a_i^*(t)a_i(t)=|a_i(t)|^2$ gives the probability of finding the system in any state i.

$$\therefore i\hbar\frac{\partial\psi}{\partial t}=\hat{H}\psi,\hat{H}=\hat{H}_0+\hat{V}(\vec{r},t),\hat{V}(\vec{r},t)=-\vec{\mu}\cdot\vec{\mathcal{E}}\text{ at }t\geq 0$$

With the wavefunction defined by (2), substitution in the Schrödinger equation gives,

$$i\hbar\frac{\partial}{\partial t}[a_1(t)\psi_1(\vec{r},t)+a_2(t)\psi_2(\vec{r},t)]=\left[\hat{H}_0+\hat{V}(\vec{r},t)\right][a_1(t)\psi_1(\vec{r},t)+a_2(t)\psi_2(\vec{r},t)]$$

$$\text{or, }i\hbar\left[\frac{da_1}{dt}\psi_1+a_1\frac{\partial\psi_1}{\partial t}+\frac{da_2}{dt}\psi_2+a_2\frac{\partial\psi_2}{\partial t}\right]=a_1\hat{H}_0\psi_1+\hat{V}a_1\psi_1+a_2\hat{H}_0\psi_2+\hat{V}a_2\psi_2\tag{3}$$

Now,

$$i\hbar\frac{\partial\psi_1(\vec{r},t)}{\partial t}=\hat{H}_0\psi_1(\vec{r},t)\qquad\text{and}\qquad i\hbar\frac{\partial\psi_2(\vec{r},t)}{\partial t}=\hat{H}_0\psi_2(\vec{r},t)$$

$$\therefore a_1i\hbar\frac{\partial\psi_1(\vec{r},t)}{\partial t}=a_1\hat{H}_0\psi_1(\vec{r},t)\qquad\qquad \therefore a_2i\hbar\frac{\partial\psi_2(\vec{r},t)}{\partial t}=a_2\hat{H}_0\psi_2(\vec{r},t)$$

From (3),

$$i\hbar\frac{da_1}{dt}\psi_1+a_1i\hbar\frac{\partial\psi_1}{\partial t}+i\hbar\frac{da_2}{dt}\psi_2+a_2i\hbar\frac{\partial\psi_2}{\partial t}=a_1\hat{H}_0\psi_1+\hat{V}a_1\psi_1+a_2\hat{H}_0\psi_2+\hat{V}a_2\psi_2$$

$$\text{or, }i\hbar\frac{da_1}{dt}\psi_1+a_1\hat{H}_0\psi_1+i\hbar\frac{da_2}{dt}\psi_2+a_2\hat{H}_0\psi_2=a_1\hat{H}_0\psi_1+\hat{V}a_1\psi_1+a_2\hat{H}_0\psi_2+\hat{V}a_2\psi_2$$

$$\text{or, }i\hbar\frac{da_1}{dt}\psi_1+i\hbar\frac{da_2}{dt}\psi_2=\hat{V}a_1\psi_1+\hat{V}a_2\psi_2$$

$$\text{or, }i\hbar\left[\frac{da_1}{dt}\psi_1+\frac{da_2}{dt}\psi_2\right]=\hat{V}a_1\psi_1+\hat{V}a_2\psi_2$$

Left multiplication of the above equation by $\phi_2^*(\vec{r})$, followed by an integration over all space gives

$$i\hbar\frac{da_1}{dt}\int\phi_2^*\psi_1\,dv+i\hbar\frac{da_2}{dt}\int\phi_2^*\psi_2\,dv=a_1\int\phi_2^*\hat{V}\psi_1\,dv+a_2\int\phi_2^*\hat{V}\psi_2\,dv$$

$$\text{or, }i\hbar\frac{da_1}{dt}\int\phi_2^*\phi_1e^{-iE_1t/\hbar}\,dv+i\hbar\frac{da_2}{dt}\int\phi_2^*\phi_2e^{-iE_2t/\hbar}\,dv$$

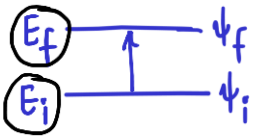
$$=a_1\int\phi_2^*\hat{V}\phi_1e^{-iE_1t/\hbar}\,dv+a_2\int\phi_2^*\hat{V}\phi_2e^{-iE_2t/\hbar}\,dv$$

$$\text{or, }i\hbar\frac{da_1}{dt}e^{-iE_1t/\hbar}\langle\phi_2|\phi_1\rangle+i\hbar\frac{da_2}{dt}e^{-iE_2t/\hbar}\langle\phi_2|\phi_2\rangle=a_1e^{-iE_1t/\hbar}\langle\phi_2|\hat{V}|\phi_1\rangle+a_2e^{-iE_2t/\hbar}\langle\phi_2|\hat{V}|\phi_2\rangle\quad(4)$$

Note that, $\langle\phi_2|\phi_1\rangle=0$ and $\langle\phi_2|\phi_2\rangle=1$, since any ϕ_i is an eigenfunction of the unperturbed Hamiltonian and the set of functions $\{\phi_n\}$ forms an orthonormal set. From (4), we therefore have,

$$i\hbar\frac{da_2}{dt}e^{-iE_2t/\hbar}=a_1e^{-iE_1t/\hbar}\langle\phi_2|\hat{V}|\phi_1\rangle+a_2e^{-iE_2t/\hbar}\langle\phi_2|\hat{V}|\phi_2\rangle$$

Application to a two-level system



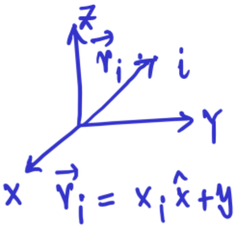
ψ_i, ψ_f : stationary states ; $\boxed{\psi_n(\vec{r},t) = \phi_n(\vec{r})\, e^{-iE_nt/\hbar}}$

$V(\vec{r})$

$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}_0 \psi$; $\hat{H}_0 \phi_n(\vec{r}) = E_n \phi_n(\vec{r})$

$\psi_n^*(\vec{r},t)\psi_n(\vec{r},t) = \phi_n^*(\vec{r})\, \underline{e}^{iE_nt/\hbar}\, \phi_n(\vec{r})\, \underline{e}^{-iE_nt/\hbar} = \phi_n^*(\vec{r})\, \phi_n(\vec{r})$

$\Rightarrow |\psi_n(\vec{r},t)|^2 = |\phi_n(\vec{r})|^2$



$\vec{r}_i = x_i\hat{x} + y_i\hat{y} + z_i\hat{z}$

q_i = point charge at i

dipole moment operator, $\hat{\vec{\mu}} = \sum_i q_i \hat{\vec{r}}_i$; $\hat{\vec{r}}_i$ = position operator at i

$\mu_x = \sum_i q_i x_i$, $\mu_y = \sum_i q_i y_i$, $\mu_z = \sum_i q_i z_i$

$\hat{\vec{\mu}}_{if} = \langle \psi_i(\vec{r},t) | \hat{\vec{\mu}} | \psi_f(\vec{r},t) \rangle$; intensity $\propto |\hat{\vec{\mu}}_{if}|^2$

Assume: an isolated molecule (no intermolecular interaction); kept in the dark
(no interaction with radiation, time-independent)

$\hat{H}_0$: Hamiltonian of the isolated molecule; time-independent

$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}_0 \psi \rightarrow$ solutions give stationary states.

$\psi_n(\vec{r},t) = \phi_n(\vec{r})\, e^{-iE_nt/\hbar}$

$\hat{H}_0 \phi_n(\vec{r}) = E_n \phi_n(\vec{r})$; $\psi_n^*(\vec{r},t)\psi_n(\vec{r},t) = \phi_n^*(\vec{r})\, e^{iE_nt/\hbar}\, \phi_n(\vec{r})\, e^{-iE_nt/\hbar} = \phi_n^*(\vec{r})\, \phi_n(\vec{r})$

$|\psi_n(\vec{r},t)|^2 = |\phi_n(\vec{r})|^2$

optical range : UV ($\lambda \sim 10^3$ Å) to IR ($\lambda \sim 10^7$ Å)

a molecule has a typical dimension of a few Å

light is constant in every part of the molecule

for a monochromatic light of freq. ν, $\vec{\mathcal{E}} = \mathcal{E}_0 \cos(2\pi\nu t) = \mathcal{E}_0 \cos\omega t$

$f(\vec{r},t)$ = electrical potential at a point $\vec{r}$ of the electric field $= -\vec{r}\cdot\vec{\mathcal{E}}$ (scalar pdt.)

$V(\vec{r},t)$ = potential energy of interaction of a point charge q in the field

$= q f(\vec{r},t)$

$\therefore$ For a system of charges, $V(\vec{r},t) = \sum_i q_i f_i(\vec{r}_i,t) = \sum_i q_i(-\vec{r}_i\cdot\vec{\mathcal{E}}) = -\sum_i q_i \vec{r}_i \cdot \vec{\mathcal{E}}_0 \cos\omega t$

or, $V(\vec{r},t) = -\sum_i \vec{\mu}_i \cdot \vec{\mathcal{E}}$ $\qquad \boxed{V(\vec{r},t) = -\vec{\mu}\cdot\vec{\mathcal{E}}}$

Say, the light source is switched on at $t=0$

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

Overall Hamiltonian, $\hat{H} = \hat{H}_0 + \underline{V(\vec{r},t)}$ at $t \geq 0$

$$\psi_n(\vec{r},t) = \phi_n(\vec{r})\,e^{-iE_nt/\hbar}$$

$$\hat{H}_0\phi_n(\vec{r}) = E_n\phi_n(\vec{r})$$

$V(\vec{r},t)$: acts as a small perturbation applied for a short span of time

$\{\phi_n(\vec{r})\}$: complete orthonormal set of functions. $\Rightarrow \langle\phi_m|\phi_n\rangle = \delta_{mn}$

$$\begin{tikzcd} & \{\phi_n(\vec{r})\} \arrow[dl] \arrow[dr] & \\ \psi_1(\vec{r},t) & & \psi_2(\vec{r},t) \end{tikzcd}$$

$$\left.\begin{aligned} \psi_1(\vec{r},t) &= \phi_1(\vec{r})\,e^{-iE_1t/\hbar} \\ \psi_2(\vec{r},t) &= \phi_2(\vec{r})\,e^{-iE_2t/\hbar} \end{aligned}\right\}$$

$\phi_1(\vec{r})$, $\phi_2(\vec{r})$ are eigenfunctions of $\hat{H}_0$ with eigenvalues E_1 and E_2.

$$i\hbar\frac{\partial\psi_1}{\partial t} = \hat{H}_0\psi_1$$

$$\text{LHS} = i\hbar\,\phi_1(\vec{r})\,e^{-iE_1t/\hbar}\left(-\frac{iE_1}{\hbar}\right) = E_1\,\phi_1(\vec{r})\,e^{-iE_1t/\hbar}$$

$$\text{RHS} = \hat{H}_0\,\phi_1(\vec{r})\,e^{-iE_1t/\hbar} = E_1\,\phi_1(\vec{r})\,e^{-iE_1t/\hbar}$$

$\therefore$ LHS = RHS

Say, at $t \geq 0$

$$\psi(\vec{r},t) = a_1(t)\,\psi_1(\vec{r},t) + a_2(t)\,\psi_2(\vec{r},t)$$

$|a_1(t)|^2$ = prob. of finding the system in state 1

$|a_2(t)|^2$ = " " " " " " 2

$$i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\psi, \quad \hat{H} = \hat{H}_0 + V(\vec{r},t), \quad V(\vec{r},t) = -\vec{\mu}\cdot\vec{\mathcal{E}}$$

or, $$i\hbar\frac{\partial}{\partial t}\left[a_1(t)\,\psi_1(\vec{r},t) + a_2(t)\,\psi_2(\vec{r},t)\right] = \left[\hat{H}_0 + V(\vec{r},t)\right]\left[a_1(t)\,\psi_1(\vec{r},t) + a_2(t)\,\psi_2(\vec{r},t)\right]$$

or, $$i\hbar\left[\frac{da_1}{dt}\psi_1 + a_1\frac{\partial\psi_1}{\partial t} + \frac{da_2}{dt}\psi_2 + a_2\frac{\partial\psi_2}{\partial t}\right] = a_1\hat{H}_0\psi_1 + Va_1\psi_1 + a_2H_0\psi_2 + Va_2\psi_2$$

$$i\hbar\frac{\partial\psi_1}{\partial t} = H_0\psi_1 \qquad i\hbar\frac{\partial\psi_2}{\partial t} = H_0\psi_2$$

$$a_1 i\hbar\frac{\partial\psi_1}{\partial t} = a_1H_0\psi_1 \qquad a_2 i\hbar\frac{\partial\psi_2}{\partial t} = a_2H_0\psi_2$$

or, $$i\hbar\frac{da_1}{dt}\psi_1 + \underbrace{\cancel{a_1 i\hbar\frac{\partial\psi_1}{\partial t}}}_{\cancel{a_1H_0\psi_1}} + i\hbar\frac{da_2}{dt}\psi_2 + \underbrace{\cancel{a_2 i\hbar\frac{\partial\psi_2}{\partial t}}}_{\cancel{a_2H_0\psi_2}} = \cancel{a_1\hat{H}_0\psi_1} + Va_1\psi_1 + \cancel{a_2H_0\psi_2} + Va_2\psi_2$$

or, $$i\hbar\frac{da_1}{dt}\psi_1 + i\hbar\frac{da_2}{dt}\psi_2 = Va_1\psi_1 + Va_2\psi_2$$ or, $$i\hbar\left[\frac{da_1}{dt}\psi_1 + \frac{da_2}{dt}\psi_2\right] = Va_1\psi_1 + Va_2\psi_2$$

Left multiplication with $\phi_2^*(\vec{r})$ and integration over all space.

$$i\hbar\left[\frac{da_1}{dt}\psi_1+\frac{da_2}{dt}\psi_2\right]=Va_1\psi_1+Va_2\psi_2$$

$$\text{or, } i\hbar\frac{da_1}{dt}\int\phi_2^*\psi_1\,d\tau+i\hbar\frac{da_2}{dt}\int\phi_2^*\psi_2\,d\tau=a_1\int\phi_2^*V\psi_1\,d\tau+a_2\int\phi_2^*V\psi_2\,d\tau$$

$$\text{or, } i\hbar\frac{da_1}{dt}\int\phi_2^*\phi_1e^{-iE_1t/\hbar}d\tau+i\hbar\frac{da_2}{dt}\int\phi_2^*\phi_2e^{-iE_2t/\hbar}d\tau=a_1\int\phi_2^*V\phi_1e^{-iE_1t/\hbar}d\tau+a_2\int\phi_2^*V\phi_2e^{-iE_2t/\hbar}d\tau$$

$$\text{or, } i\hbar\frac{da_1}{dt}e^{-iE_1t/\hbar}\underbrace{\langle\phi_2|\phi_1\rangle}_{=0}+i\hbar\frac{da_2}{dt}e^{-iE_2t/\hbar}\underbrace{\langle\phi_2|\phi_2\rangle}_{=1}=a_1e^{-iE_1t/\hbar}\langle\phi_2|V|\phi_1\rangle+a_2e^{-iE_2t/\hbar}\langle\phi_2|V|\phi_2\rangle$$

$$\text{or, } i\hbar\frac{da_2}{dt}e^{-iE_2t/\hbar}=a_1e^{-iE_1t/\hbar}\langle\phi_2|V|\phi_1\rangle+a_2e^{-iE_2t/\hbar}\langle\phi_2|V|\phi_2\rangle$$

$$\text{or, } i\hbar\frac{da_2}{dt}=a_1e^{i(E_2-E_1)t/\hbar}\langle\phi_2|V|\phi_1\rangle+a_2\langle\phi_2|V|\phi_2\rangle$$

18/10/2024

$$\therefore i\hbar\frac{da_2}{dt}=a_1e^{i(E_2-E_1)t/\hbar}\langle\phi_2|V|\phi_1\rangle+\boxed{a_2\langle\phi_2|V|\phi_2\rangle}$$

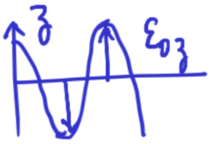
$\psi_n(\vec r,t)=\phi_n(\vec r)\,e^{-iE_nt/\hbar}$

* System initially $(t=0)$ in the state $\psi_1 \Rightarrow a_1(t=0)=a_1(0)=1$
$a_2(t=0)=a_2(0)=0$

* Perturbation $V(\vec r,t)$ is small; values of a_1 and a_2 at any time $t\geq 0$ do not differ much from their values at $t=0$.

$$\therefore i\hbar\frac{da_2}{dt}=e^{i(E_2-E_1)t/\hbar}\langle\phi_2|V|\phi_1\rangle\ ;\ V(\vec r,t)=-\hat{\vec\mu}\cdot\vec{\mathcal{E}}$$

$$\text{or, } i\hbar\frac{da_2}{dt}=-e^{i(E_2-E_1)t/\hbar}\langle\phi_2|\hat{\vec\mu}\cdot\vec{\mathcal{E}}|\phi_1\rangle=-e^{i(E_2-E_1)t/\hbar}\langle\phi_2|\hat{\vec\mu}\cdot\vec{\mathcal{E}}_0\cos(2\pi\nu t)|\phi_1\rangle$$



$$\text{or, } i\hbar\frac{da_2}{dt}=-e^{i(E_2-E_1)t/\hbar}\cos(2\pi\nu t)\langle\phi_2|\hat{\vec\mu}\cdot\vec{\mathcal{E}}_0|\phi_1\rangle$$

Considering the z-component only

$$\therefore i\hbar\frac{da_2}{dt}=-e^{i(E_2-E_1)t/\hbar}\cos(2\pi\nu t)\langle\phi_2|\mu_z\mathcal{E}_{0z}|\phi_1\rangle$$
$$=-e^{i(E_2-E_1)t/\hbar}\cos(2\pi\nu t)\,\mathcal{E}_{0z}\langle\phi_2|\mu_z|\phi_1\rangle$$

Say, $\langle\phi_2|\mu_z|\phi_1\rangle=(\mu_z)_{21}$ $\quad\therefore i\hbar\dfrac{da_2}{dt}=-e^{i(E_2-E_1)t/\hbar}\cos(2\pi\nu t)(\mu_z)_{21}\mathcal{E}_{0z}$

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-18, 18/10/2024)

$$\left.\begin{array}{l} e^{i\theta} = \cos\theta + i\sin\theta \\ e^{-i\theta} = \cos\theta - i\sin\theta \end{array}\right\} \begin{array}{l} e^{i\theta} + e^{-i\theta} = 2\cos\theta \Rightarrow \cos\theta = \frac{1}{2}(e^{i\theta} + e^{-i\theta}) \\ \cos(2\pi\nu t) = \frac{1}{2}(e^{i2\pi\nu t} + e^{-i2\pi\nu t}) \end{array}$$

$$\therefore i\hbar \frac{da_2}{dt} = -e^{i(E_2-E_1)t/\hbar}\, \frac{1}{2}\left(e^{i2\pi\nu t} + e^{-i2\pi\nu t}\right)(\mu_z)_{21}\varepsilon_{0z}$$

$$= -\frac{1}{2}(\mu_z)_{21}\varepsilon_{0z}\left[e^{i(E_2-E_1+h\nu)t/\hbar} + e^{i(E_2-E_1-h\nu)t/\hbar}\right]$$

$$\text{or, } i\hbar\, da_2 = -\frac{1}{2}(\mu_z)_{21}\varepsilon_{0z}\left[e^{i(E_2-E_1+h\nu)t/\hbar} + e^{i(E_2-E_1-h\nu)t/\hbar}\right]dt$$

Integrating from $t=0$ to $t=t'$

$$\therefore i\hbar\left[a_2(t') - a_2(0)\right] = -\frac{1}{2}(\mu_z)_{21}\varepsilon_{0z}\left[\frac{e^{i(E_2-E_1+h\nu)t/\hbar}}{i(E_2-E_1+h\nu)/\hbar} + \frac{e^{i(E_2-E_1-h\nu)t/\hbar}}{i(E_2-E_1-h\nu)/\hbar}\right]_0^{t'}$$

$$\text{or, } i\hbar\, a_2(t') = -\frac{1}{2}(\mu_z)_{21}\varepsilon_{0z}\frac{\hbar}{i}\left[\frac{e^{i(E_2-E_1+h\nu)t/\hbar}}{E_2-E_1+h\nu} + \frac{e^{i(E_2-E_1-h\nu)t/\hbar}}{E_2-E_1-h\nu}\right]_0^{t'}$$

$$\text{or, } a_2(t') = \frac{1}{2}(\mu_z)_{21}\varepsilon_{0z}\left[\frac{e^{i(E_2-E_1+h\nu)t'/\hbar} - 1}{E_2-E_1+h\nu} + \boxed{\frac{e^{i(E_2-E_1-h\nu)t'/\hbar} - 1}{E_2-E_1-h\nu}}\right]$$

Extremely large

$\boxed{E_2 - E_1 \cong h\nu}$ (Bohr frequency condition)
resonance condition

$$a_2(t') \cong \frac{1}{2}(\mu_z)_{21}\varepsilon_{0z}\frac{\left[e^{i(E_2-E_1-h\nu)t'/\hbar} - 1\right]}{E_2-E_1-h\nu}$$

$|a_2(t')|^2$ = probability of finding the system in state 2 as a result of the transition

$$\therefore |a_2(t')|^2 = \frac{1}{4}(\mu_z)_{21}^2\varepsilon_{0z}^2\frac{\left|e^{i(E_2-E_1-h\nu)t'/\hbar} - 1\right|^2}{(E_2-E_1-h\nu)^2}$$

$$|e^{i\theta} - 1|^2 = (e^{i\theta} - 1)^*(e^{i\theta} - 1) = (e^{-i\theta} - 1)(e^{i\theta} - 1) = (1 - e^{i\theta})(1 - e^{-i\theta}) = 1 - e^{-i\theta} - e^{i\theta} + 1$$

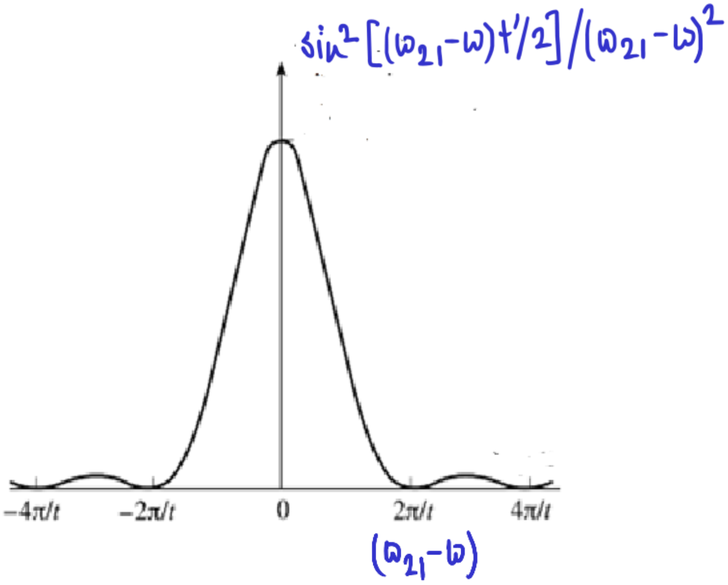
$$= 2 - (e^{i\theta} + e^{-i\theta}) = 2 - 2\cos\theta = 2(1 - \cos\theta) = 4\sin^2(\theta/2)$$

$$\therefore |a_2(t')|^2 = \frac{1}{4}(\mu_z)_{21}^2\varepsilon_{0z}^2\frac{4\sin^2[(E_2-E_1-h\nu)t'/2\hbar]}{(E_2-E_1-h\nu)^2} = (\mu_z)_{21}^2\varepsilon_{0z}^2\frac{\sin^2[(E_2-E_1-h\nu)t'/2\hbar]}{(E_2-E_1-h\nu)^2}$$

$$E_2 - E_1 = \hbar\omega_{21};\ h\nu = \hbar\omega$$

$$\therefore |a_2(t')|^2 = (\mu_z)_{21}^2\varepsilon_{0z}^2\frac{\sin^2[(\hbar\omega_{21}-\hbar\omega)t'/2\hbar]}{(\hbar\omega_{21}-\hbar\omega)^2} = (\mu_z)_{21}^2(\varepsilon_{0z}^2/\hbar^2)\frac{\sin^2[(\omega_{21}-\omega)t'/2]}{(\omega_{21}-\omega)^2}$$

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-18, 18/10/2024)



Application to a two-level system

Let us think of an atom/molecule, which, for simplicity, we will treat as a two-level system to maintain a simplicity of our formal treatment. The system is initially isolated (no interatomic/intermolecular interactions), and is kept in the dark (no interaction with light/electromagnetic waves). Such an initial state of the system is defined well by the zeroth-order/unperturbed Hamiltonian $\hat{H}_0$ and satisfies the Schrödinger equation

$$i\hbar\frac{\partial\psi}{\partial t} = \hat{H}_0\psi \tag{7.1}$$

The solutions of the above equation are the stationary states

$$\psi_n(\vec{r},t) = \phi_n(\vec{r})e^{-iE_nt/\hbar}$$

such that, $\hat{H}_0\phi_n(\vec{r}) = E_n\phi_n(\vec{r})$, with the property that

$$\psi_n^*(\vec{r},t)\psi_n(\vec{r},t) = \phi_n^*(\vec{r})e^{iE_nt/\hbar}\phi_n(\vec{r})e^{-iE_nt/\hbar} = \phi_n^*(\vec{r})\phi_n(\vec{r}) \Rightarrow |\psi_n(\vec{r},t)|^2 = |\phi_n(\vec{r})|^2$$

Now let us consider the interaction of this system with light/electromagnetic radiation (of optical range, UV to IR, with the wavelength spanning from $\sim 10^3$Å to $\sim 10^7$Å), having an electric field $\vec{\mathcal{E}}$ and a magnetic field $\vec{B}$. Since the interaction of the atomic/molecular electrons with $\vec{\mathcal{E}}$ is much stronger than all other interactions, we take into consideration this interaction only, and treat all others as hyperfine interactions. A typical molecule has a dimension of a few Å. Hence, for all practical purposes, light is assumed to be homogeneous in every part of the molecule. For a monochromatic light of frequency ν,

$$\vec{\mathcal{E}} = \vec{\mathcal{E}}_0\cos(2\pi\nu t) = \vec{\mathcal{E}}_0\cos\omega t$$

The electrons of the atom/molecule interact with $\vec{\mathcal{E}}$ of light along the direction of $\vec{\mathcal{E}}$. Say, $f(\vec{r},t)$ is the electrical potential of the electric field at a point $\vec{r}$ in space. Hence, $f(\vec{r},t)$ is given by the scalar product

$$f(\vec{r},t) = -\vec{r}\cdot\vec{\mathcal{E}}$$

If $V(\vec{r},t)$ is the potential energy of interaction of a point charge q with the electric field $\vec{\mathcal{E}}$, then

$$V(\vec{r},t) = qf(\vec{r},t)$$

However, our system is essentially a system of such point charges (electrons), and

$$V(\vec{r},t) = \sum_i q_i f_i(\vec{r},t) = \sum_i q_i\left(-\vec{r}\cdot\vec{\mathcal{E}}\right) = -\sum_i q_i\vec{r}_i\cdot\vec{\mathcal{E}} = -\sum_i \vec{\mu}_i\cdot\vec{\mathcal{E}}$$

Hence, for our treatment, the light source acts as the perturbation, and the corresponding perturbation potential has the form $\hat{V}(\vec{r},t) = -\vec{\mu}\cdot\vec{\mathcal{E}}$. We assume that we switch on the light source (perturbation) at $t = 0$, and that $\hat{V}(\vec{r},t)$ acts as a small perturbation, so that the time-dependent perturbation theory is applicable. Therefore, at all times $t \geq 0$, the Hamiltonian for the system becomes

$$\hat{H} = \hat{H}_0 + \hat{V}(\vec{r},t) \text{ at } t \geq 0$$

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-18, 18/10/2024)

We also recall that; the unperturbed system is defined by (7.1) in a manner such that $\hat{H}_0\phi_n(\vec{r}) = E_n\phi_n(\vec{r})$ and the stationary states are given by $\psi_n(\vec{r},t) = \phi_n(\vec{r})e^{-iE_nt/\hbar}$. Our system has an infinite number of stationary states, and $\{\phi_n(\vec{r})\}$ spans a complete orthonormal set of functions. To preserve the simplicity of our derivation, we assume that our molecule has only two stationary states, $\psi_1(\vec{r},t)$ and $\psi_2(\vec{r},t)$, such that,

$$\psi_1(\vec{r},t) = \phi_1(\vec{r})e^{-iE_1t/\hbar}, \psi_2(\vec{r},t) = \phi_2(\vec{r})e^{-iE_2t/\hbar}$$

$\phi_1(\vec{r})$ and $\phi_2(\vec{r})$ are the eigenfunctions of $\hat{H}_0$. We solve

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

Does the Schrödinger equation get satisfied with $\hat{H}_0$ and the above forms of $\psi_1(\vec{r},t)$ and $\psi_2(\vec{r},t)$?

Let us check with $\psi_1(\vec{r},t)$, where $\psi_1(\vec{r},t) = \phi_1(\vec{r})e^{-iE_1t/\hbar}$. Hence,

$$i\hbar\frac{\partial}{\partial t}\phi_1(\vec{r})e^{-iE_1t/\hbar} = \hat{H}_0\phi_1(\vec{r})e^{-iE_1t/\hbar}$$

$$\therefore \text{LHS} = i\hbar\phi_1(\vec{r})e^{-iE_1t/\hbar}\left(-\frac{iE_1}{\hbar}\right) = E_1\phi_1(\vec{r})e^{-iE_1t/\hbar} \text{ and RHS} = E_1\phi_1(\vec{r})e^{-iE_1t/\hbar}$$

$$\Rightarrow \text{LHS} = \text{RHS}$$

One may verify with $\phi_2(\vec{r})$ in the same manner.

Say, the system is initially (at $t = 0$) in state ψ_1. Hence, the initial state wavefunction for the system is given by $\psi_1(\vec{r},t)$. At $t = 0$, the light source is switched on. For any time $t \geq 0$, $\psi_1(\vec{r},t)$ is not an eigenfunction of $\hat{H}$. Say, at $t \geq 0$, the wavefunction has the form

$$\psi(\vec{r},t) = a_1(t)\psi_1(\vec{r},t) + a_2(t)\psi_2(\vec{r},t) \tag{7.2}$$

where a_1 and a_2 are the combining coefficients and are functions of t only, while ψ_1, ψ_2 and $\hat{V}$ are functions of both space and time. We note that, any $a_i^*(t)a_i(t) = |a_i(t)|^2$ gives the probability of finding the system in any state i.

$$\therefore i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\psi, \hat{H} = \hat{H}_0 + \hat{V}(\vec{r},t), \hat{V}(\vec{r},t) = -\vec{\mu}\cdot\vec{\mathcal{E}} \text{ at } t \geq 0$$

With the wavefunction defined by (7.2), substitution in the Schrödinger equation gives,

$$i\hbar\frac{\partial}{\partial t}[a_1(t)\psi_1(\vec{r},t) + a_2(t)\psi_2(\vec{r},t)] = \left[\hat{H}_0 + \hat{V}(\vec{r},t)\right][a_1(t)\psi_1(\vec{r},t) + a_2(t)\psi_2(\vec{r},t)]$$

$$\text{or, } i\hbar\left[\frac{da_1}{dt}\psi_1 + a_1\frac{\partial\psi_1}{\partial t} + \frac{da_2}{dt}\psi_2 + a_2\frac{\partial\psi_2}{\partial t}\right] = a_1\hat{H}_0\psi_1 + \hat{V}a_1\psi_1 + a_2\hat{H}_0\psi_2 + \hat{V}a_2\psi_2 \tag{7.3}$$

Now,

$$i\hbar\frac{\partial\psi_1(\vec{r},t)}{\partial t} = \hat{H}_0\psi_1(\vec{r},t) \qquad \text{and} \qquad i\hbar\frac{\partial\psi_2(\vec{r},t)}{\partial t} = \hat{H}_0\psi_2(\vec{r},t)$$

$$\therefore a_1 i\hbar\frac{\partial\psi_1(\vec{r},t)}{\partial t} = a_1\hat{H}_0\psi_1(\vec{r},t) \qquad \therefore a_2 i\hbar\frac{\partial\psi_2(\vec{r},t)}{\partial t} = a_2\hat{H}_0\psi_2(\vec{r},t)$$

From (7.3),

$$i\hbar\frac{da_1}{dt}\psi_1 + a_1 i\hbar\frac{\partial\psi_1}{\partial t} + i\hbar\frac{da_2}{dt}\psi_2 + a_2 i\hbar\frac{\partial\psi_2}{\partial t} = a_1\hat{H}_0\psi_1 + \hat{V}a_1\psi_1 + a_2\hat{H}_0\psi_2 + \hat{V}a_2\psi_2$$

$$\text{or, } i\hbar\frac{da_1}{dt}\psi_1 + a_1\hat{H}_0\psi_1 + i\hbar\frac{da_2}{dt}\psi_2 + a_2\hat{H}_0\psi_2 = a_1\hat{H}_0\psi_1 + \hat{V}a_1\psi_1 + a_2\hat{H}_0\psi_2 + \hat{V}a_2\psi_2$$

$$\text{or, } i\hbar\frac{da_1}{dt}\psi_1 + i\hbar\frac{da_2}{dt}\psi_2 = \hat{V}a_1\psi_1 + \hat{V}a_2\psi_2$$

$$\text{or, } i\hbar\left[\frac{da_1}{dt}\psi_1 + \frac{da_2}{dt}\psi_2\right] = \hat{V}a_1\psi_1 + \hat{V}a_2\psi_2$$

Left multiplication of the above equation by $\phi_2^*(\vec{r})$, followed by an integration over all space gives

$$i\hbar\frac{da_1}{dt}\int\phi_2^*\psi_1\,dv + i\hbar\frac{da_2}{dt}\int\phi_2^*\psi_2\,dv = a_1\int\phi_2^*\hat{V}\psi_1\,dv + a_2\int\phi_2^*\hat{V}\psi_2\,dv$$

$$\text{or, } i\hbar\frac{da_1}{dt}\int\phi_2^*\phi_1 e^{-iE_1t/\hbar}\,dv + i\hbar\frac{da_2}{dt}\int\phi_2^*\phi_2 e^{-iE_2t/\hbar}\,dv$$

$$= a_1\int\phi_2^*\hat{V}\phi_1 e^{-iE_1t/\hbar}\,dv + a_2\int\phi_2^*\hat{V}\phi_2 e^{-iE_2t/\hbar}\,dv$$

$$\text{or, } i\hbar\frac{da_1}{dt}e^{-iE_1t/\hbar}\langle\phi_2|\phi_1\rangle + i\hbar\frac{da_2}{dt}e^{-iE_2t/\hbar}\langle\phi_2|\phi_2\rangle = a_1e^{-iE_1t/\hbar}\langle\phi_2|\hat{V}|\phi_1\rangle + a_2e^{-iE_2t/\hbar}\langle\phi_2|\hat{V}|\phi_2\rangle \quad (7.4)$$

Note that, $\langle\phi_2|\phi_1\rangle = 0$ and $\langle\phi_2|\phi_2\rangle = 1$, since any ϕ_i is an eigenfunction of the unperturbed Hamiltonian and the set of functions $\{\phi_n\}$ forms an orthonormal set. From (7.4), we therefore have,

$$i\hbar\frac{da_2}{dt}e^{-iE_2t/\hbar} = a_1e^{-iE_1t/\hbar}\langle\phi_2|\hat{V}|\phi_1\rangle + a_2e^{-iE_2t/\hbar}\langle\phi_2|\hat{V}|\phi_2\rangle$$

Since the system was initially in the state ψ_1, $a_1(t=0) = a_1(0) = 1$ and $a_2(t=0) = a_2(0) = 0$. Also, as the perturbation is small, the values of a_1 and a_2 at any time $t \geq 0$ do not differ much from their values at $t = 0$ (when there was no perturbation).

$$\therefore\ i\hbar\frac{da_2}{dt} = e^{i(E_2-E_1)t/\hbar}\langle\phi_2|\hat{V}|\phi_1\rangle \text{ with } \hat{V}(\vec{r},t) = -\vec{\mu}\cdot\vec{\mathcal{E}}$$

$$\text{or, } i\hbar\frac{da_2}{dt} = -e^{i(E_2-E_1)t/\hbar}\langle\phi_2|\vec{\mu}\cdot\vec{\mathcal{E}}|\phi_1\rangle$$

$$\text{or, } i\hbar\frac{da_2}{dt} = -e^{i(E_2-E_1)t/\hbar}\langle\phi_2|\vec{\mu}\cdot\vec{\mathcal{E}}_0\cos(2\pi\nu t)\,|\phi_1\rangle$$

$$\text{or, } i\hbar\frac{da_2}{dt} = -e^{i(E_2-E_1)t/\hbar}\cos(2\pi\nu t)\,\langle\phi_2|\vec{\mu}\cdot\vec{\mathcal{E}}_0|\phi_1\rangle$$

Let us consider the z-component of the electric field only, so that

$$i\hbar\frac{da_2}{dt} = -e^{i(E_2-E_1)t/\hbar}\cos(2\pi\nu t)\,\langle\phi_2|\mu_z\mathcal{E}_{0z}|\phi_1\rangle$$

For a constant electric field, $\mathcal{E}_{0z}$ is a constant, and may be taken out of the integral, giving

$$i\hbar\frac{da_2}{dt} = -e^{i(E_2-E_1)t/\hbar}\cos(2\pi\nu t)\,\mathcal{E}_{0z}\langle\phi_2|\mu_z|\phi_1\rangle$$

Say, we define $\langle\phi_2|\mu_z|\phi_1\rangle = (\mu_z)_{21}$, the transition dipole moment integral for the transition 1 → 2.

$$\therefore\ i\hbar\frac{da_2}{dt} = -e^{i(E_2-E_1)t/\hbar}\cos(2\pi\nu t)\,\mathcal{E}_{0z}(\mu_z)_{21} \quad (7.5)$$

Now, $e^{i\theta} = \cos\theta + i\sin\theta$ and $e^{-i\theta} = \cos\theta - i\sin\theta$, so that, $e^{i\theta} + e^{-i\theta} = 2\cos\theta$.

$$\therefore\ \cos\theta = \frac{1}{2}\left(e^{i\theta} + e^{-i\theta}\right)$$

From (7.5), we have

$$i\hbar\frac{da_2}{dt} = -\frac{1}{2}(\mu_z)_{21}\mathcal{E}_{0z}\left(e^{i2\pi\nu t} + e^{-i2\pi\nu t}\right)e^{i(E_2-E_1)t/\hbar}$$

$$i\hbar\frac{da_2}{dt} = -\frac{1}{2}(\mu_z)_{21}\mathcal{E}_{0z}\left(e^{i2\pi\nu t} + e^{-i2\pi\nu t}\right)e^{i(E_2-E_1)t/\hbar}$$

$$\text{or, } i\hbar\frac{da_2}{dt} = -\frac{1}{2}(\mu_z)_{21}\mathcal{E}_{0z}\left(e^{ih\nu t/\hbar} + e^{-ih\nu t/\hbar}\right)e^{i(E_2-E_1)t/\hbar}$$

$$\text{or, } i\hbar\frac{da_2}{dt} = -\frac{1}{2}(\mu_z)_{21}\mathcal{E}_{0z}[\exp\{i(E_2 - E_1 + h\nu)t/\hbar\} + \exp\{i(E_2 - E_1 - h\nu)t/\hbar\}]$$

$$\text{or, } i\hbar da_2 = -\frac{1}{2}(\mu_z)_{21}\mathcal{E}_{0z}[\exp\{i(E_2 - E_1 + h\nu)t/\hbar\} + \exp\{i(E_2 - E_1 - h\nu)t/\hbar\}]dt$$

Integrating from 0 to t',

$$i\hbar[a_2(t') - a_2(0)] = -\frac{1}{2}(\mu_z)_{21}\mathcal{E}_{0z}\left[\frac{\exp\{i(E_2 - E_1 + h\nu)t/\hbar\}}{i(E_2 - E_1 + h\nu)/\hbar} + \frac{\exp\{i(E_2 - E_1 - h\nu)t/\hbar\}}{i(E_2 - E_1 - h\nu)/\hbar}\right]_0^{t'}$$

Now, $a_2(0) = a_2(t=0) = 0$, since the system was initially in the state ψ_1.

$$\therefore\ i\hbar a_2(t') = -\frac{1}{2}(\mu_z)_{21}\mathcal{E}_{0z}\left(\frac{\hbar}{i}\right)\left[\frac{\exp\{i(E_2 - E_1 + h\nu)t/\hbar\}}{E_2 - E_1 + h\nu} + \frac{\exp\{i(E_2 - E_1 - h\nu)t/\hbar\}}{E_2 - E_1 - h\nu}\right]_0^{t'}$$

$$\text{or, } a_2(t') = \frac{1}{2}(\mu_z)_{21}\mathcal{E}_{0z}\left[\frac{\exp\{i(E_2 - E_1 + h\nu)t/\hbar\}}{E_2 - E_1 + h\nu} + \frac{\exp\{i(E_2 - E_1 - h\nu)t/\hbar\}}{E_2 - E_1 - h\nu}\right]_0^{t'}$$

$$\text{or, } a_2(t') = \frac{1}{2}(\mu_z)_{21}\mathcal{E}_{0z}\left[\frac{\exp\{i(E_2 - E_1 + h\nu)t'/\hbar\} - 1}{E_2 - E_1 + h\nu} + \frac{\exp\{i(E_2 - E_1 - h\nu)t'/\hbar\} - 1}{E_2 - E_1 - h\nu}\right] \quad (7.6)$$

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-18, 18/10/2024)

The transition 1 → 2 takes place only when $E_2 - E_1 \approx h\nu$ (the Bohr frequency condition, or the resonance condition, in spectroscopy). Under this condition, the second term within the square brackets on the RHS of (7.6) is the dominant term, and is in magnitude much larger as compared to the other term.

$$\therefore a_2(t') \approx \frac{1}{2}(\mu_z)_{21}\mathcal{E}_{0z}\left[\frac{\exp\{i(E_2 - E_1 - h\nu)t'/\hbar\} - 1}{E_2 - E_1 - h\nu}\right]$$

$$\text{or, } |a_2(t')|^2 \approx \frac{1}{4}(\mu_z)_{21}^2\mathcal{E}_{0z}^2\frac{|\exp\{i(E_2 - E_1 - h\nu)t'/\hbar\} - 1|^2}{(E_2 - E_1 - h\nu)^2} \qquad (7.7)$$

Now, $|a_2(t')|^2$ gives the probability of finding the system in the state 2 as a result of the transition 1 → 2.

Now, to simplify (7.7), we use the following identity.

$$\left|e^{i\theta} - 1\right|^2 = \left(e^{i\theta} - 1\right)^*\left(e^{i\theta} - 1\right) = \left(e^{-i\theta} - 1\right)\left(e^{i\theta} - 1\right) = \left(1 - e^{i\theta}\right)\left(1 - e^{-i\theta}\right)$$

$$\text{or, } \left|e^{i\theta} - 1\right|^2 = 1 - e^{-i\theta} - e^{i\theta} + 1 = 2 - \left(e^{i\theta} + e^{-i\theta}\right) = 2 - 2\cos\theta = 2(1 - \cos\theta)$$

$$\text{or, } \left|e^{i\theta} - 1\right|^2 = 2 \times 2\sin^2(\theta/2) = 4\sin^2(\theta/2)$$

Hence, from (7.7), we have

$$|a_2(t')|^2 \approx \frac{1}{4}(\mu_z)_{21}^2\mathcal{E}_{0z}^2\frac{4\sin^2[(E_2 - E_1 - h\nu)t'/2\hbar]}{(E_2 - E_1 - h\nu)^2} = (\mu_z)_{21}^2\mathcal{E}_{0z}^2\frac{\sin^2[(E_2 - E_1 - h\nu)t'/2\hbar]}{(E_2 - E_1 - h\nu)^2} \qquad (7.8)$$

We will use (7.8), or one of its more general forms, to understand the intensities of spectroscopic transitions.

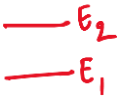
GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-19, 19/10/2024)

From the last class,

$|n\rangle \rightarrow |m\rangle$

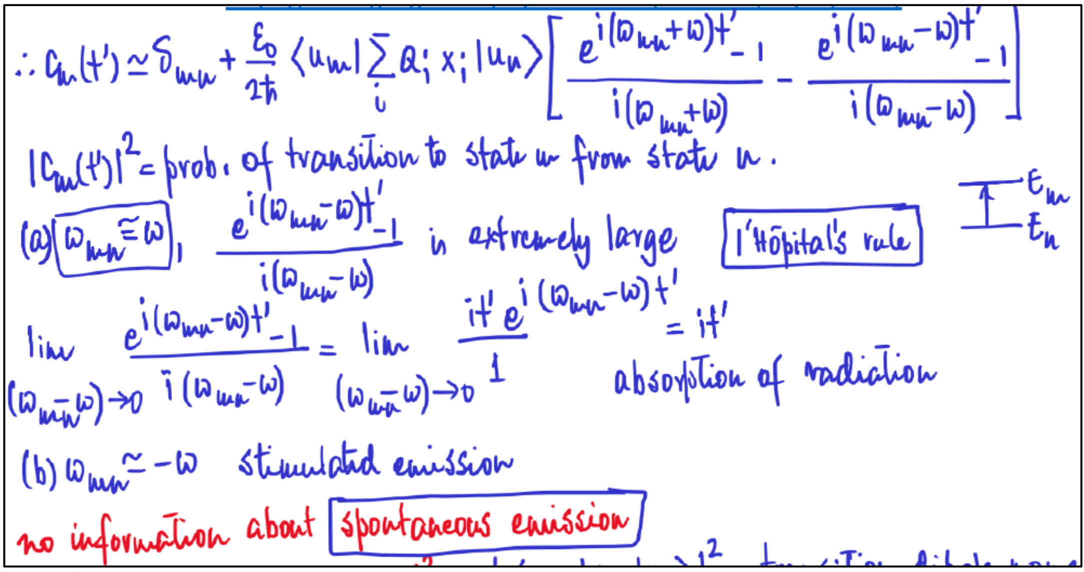
$$|a_2(t')|^2 \cong (\mu_z)_{21}^2 (\mathcal{E}_{0z}/\hbar)^2 \frac{\sin^2[(\omega_{21}-\omega)t'/2]}{(\omega_{21}-\omega)^2}, \text{ where } (\mu_z)_{21} = \boxed{\langle \phi_2|\mu_z|\phi_1\rangle}$$

appears from the integral over $V(\vec{r},t)$



For any general transition from state $|n\rangle$ to $|m\rangle$, the probability that the system would be found in state $|m\rangle$ as a result of the transition will be

$$|c_m(t')|^2 \cong \frac{\mathcal{E}_0^2}{\hbar^2}|V_{mn}|^2 \frac{\sin^2[(\omega_{mn}-\omega)t'/2]}{(\omega_{mn}-\omega)^2} = \frac{\mathcal{E}_0^2}{4\hbar^2}|V_{mn}|^2 \frac{\sin^2[(\omega_{mn}-\omega)t'/2]}{[(\omega_{mn}-\omega)/2]^2}$$



$$\therefore c_m(t') \simeq \delta_{mn} + \frac{\mathcal{E}_0}{2\hbar}\langle u_m|\sum_i Q_i x_i|u_n\rangle \left[\frac{e^{i(\omega_{mn}+\omega)t'}-1}{i(\omega_{mn}+\omega)} - \frac{e^{i(\omega_{mn}-\omega)t'}-1}{i(\omega_{mn}-\omega)}\right]$$

$|c_m(t')|^2$ = prob. of transition to state m from state n.

(a) $\boxed{\omega_{mn} \cong \omega}$, $\frac{e^{i(\omega_{mn}-\omega)t'}-1}{i(\omega_{mn}-\omega)}$ is extremely large $\boxed{\text{l'Hôpital's rule}}$

E_m
E_n

$$\lim_{(\omega_{mn}-\omega)\to 0} \frac{e^{i(\omega_{mn}-\omega)t'}-1}{i(\omega_{mn}-\omega)} = \lim_{(\omega_{mn}-\omega)\to 0} \frac{it' e^{i(\omega_{mn}-\omega)t'}}{1} = it'$$

absorption of radiation

(b) $\omega_{mn} \cong -\omega$ stimulated emission

no information about $\boxed{\text{spontaneous emission}}$

from Class-16 (14/10/2024)

* TDPT accounts for absorption of radiation ($\omega_{mn} \cong \omega$)

* TDPT accounts for stimulated emission ($\omega_{mn} \cong -\omega$)

* TDPT does not account for spontaneous emission.

$\omega_{mn} \cong \omega$ absorption of radiation

$\omega_{mn} \cong -\omega$ emission of radiation (stimulated emission)

Limitation of ordinary TDPT: absence of any information of spontaneous emission.

Einstein: invoke photon concept of radiation

$\omega_{mn} = 2\pi\nu_{mn}$

$\omega = 2\pi\nu$

$$|c_m(t')|^2 = \frac{\mathcal{E}_0^2}{4}\left(\frac{|V_{mn}|}{\hbar}\right)^2 \frac{\sin^2[(\omega_{mn}-\omega)t'/2]}{[(\omega_{mn}-\omega)/2]^2}$$

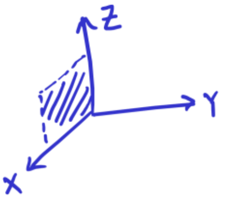
$$\therefore \frac{\sin^2[(\omega_{mn}-\omega)t'/2]}{[(\omega_{mn}-\omega)/2]^2} = \frac{\sin^2[2\pi(\nu_{mn}-\nu)t'/2]}{[2\pi(\nu_{mn}-\nu)/2]^2} = \frac{\sin^2[\pi(\nu_{mn}-\nu)t']}{\pi^2(\nu_{mn}-\nu)^2}$$

$$\therefore |c_m(t')|^2 = \left(\frac{\mathcal{E}_0|V_{mn}|}{\hbar}\right)^2 \frac{\sin^2[\pi(\nu_{mn}-\nu)t']}{4\pi^2(\nu_{mn}-\nu)^2}$$

Say, $\rho(\nu)$ = energy density of the radiation field (amount of energy per unit volume whose freq. lies within the range of ν to $\nu + d\nu$)

$\rho(\nu)$ has the units of $J\ m^{-3}$.

$$\rho(\nu) = \frac{\epsilon_0}{2}\mathcal{E}_0^2 \text{, where, } \epsilon_0 = \text{permittivity of free space} = 8.8 \times 10^{-12}\ C^2 N^{-1} m^{-2}$$



For an x-polarized radiation, moving along z-axis

$$\underline{\rho_z(\nu)} = \epsilon_0 \mathcal{E}_0^2/2 \quad \Rightarrow \mathcal{E}_0^2 = 2\rho_z(\nu)/\epsilon_0$$

↓ energy density for only that fraction of the photons which move along the z-axis.

$$\therefore |C_m(t')|^2 = \frac{2\rho_z(\nu)}{\epsilon_0}\left(\frac{|V_{mn}|}{\hbar}\right)^2 \frac{\sin^2[\pi(\nu_{mn}-\nu)t']}{4\pi^2(\nu_{mn}-\nu)^2}$$

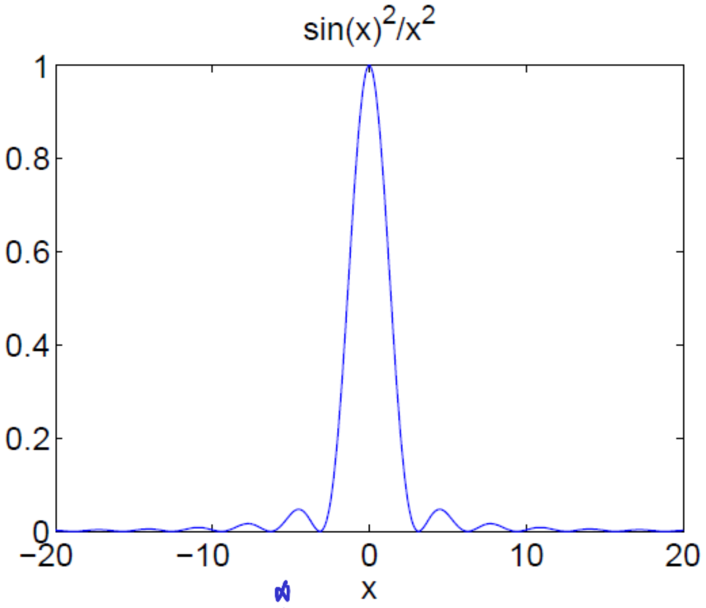
For a volume having an isotropic (same in all directions) distribution of radiation

$$\rho_z(\nu) = \frac{1}{3}\rho(\nu)$$

$$\therefore |C_m(t')|^2 = \frac{2\rho(\nu)|V_{mn}|^2}{3\epsilon_0\hbar^2}\frac{\sin^2[\pi(\nu_{mn}-\nu)t']}{4\pi^2(\nu_{mn}-\nu)^2} = \frac{t'^2\, 2\rho(\nu)|V_{mn}|^2}{3\epsilon_0\hbar^2}\frac{\sin^2[\pi(\nu_{mn}-\nu)t']}{4\pi^2(\nu_{mn}-\nu)^2 t'^2}$$

Say, $x = \pi(\nu_{mn}-\nu)t'$

$$\therefore |C_m(t')|^2 = \frac{t'^2\rho(\nu)|V_{mn}|^2}{6\epsilon_0\hbar^2}\frac{\sin^2 x}{x^2} \qquad \frac{t'^2}{x^2} = \frac{\cancel{t'^2}}{\pi^2(\nu_{mn}-\nu)^2\cancel{t'^2}}$$



- * $\frac{\sin^2 x}{x^2}$ is sharply peaked at $x=0$.
- * domain of the function $-\infty < x < \infty$
  important contribution: $-\pi < x < \pi$
- * if $t' > |\nu_{mn}-\nu|^{-1}$, $|C_m(t')|^2$ will be quite small.

$\underline{\nu \cong \nu_{mn}}$; $x = \pi(\nu_{mn}-\nu)t'$

Bohr freq. condition

$$\langle |C_m(t')|^2 \rangle = \int_0^\infty |C_m(t')|^2 d\nu \qquad \therefore \langle |C_m(t')|^2 \rangle = \frac{t'^2|V_{mn}|^2}{6\epsilon_0\hbar^2}\int_0^\infty \frac{\rho(\nu)\sin^2 x}{x^2} d\nu$$

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-19, 19/10/2024)

From our previous discussions, we have seen that

$$|a_2(t')|^2 \approx \frac{1}{4}(\mu_z)_{21}^2\mathcal{E}_{0z}^2\frac{4\sin^2[(E_2-E_1-h\nu)t'/2\hbar]}{(E_2-E_1-h\nu)^2} = (\mu_z)_{21}^2\mathcal{E}_{0z}^2\frac{\sin^2[(E_2-E_1-h\nu)t'/2\hbar]}{(E_2-E_1-h\nu)^2}$$

We may simplify the above expression to get

$$|a_2(t')|^2 = (\mu_z)_{21}^2(\mathcal{E}_{0z}/\hbar)^2\frac{\sin^2[(\omega_{21}-\omega)t'/2]}{(\omega_{21}-\omega)^2}, \text{where } (\mu_z)_{21} = \langle\phi_2|\mu_z|\phi_1\rangle$$

We recall that the integral $(\mu_z)_{21} = \langle\phi_2|\mu_z|\phi_1\rangle$ appears from the integral over the perturbation, as emphasized in our earlier discussions. Now, generalizing $|a_2(t')|^2$ for any arbitrary situation,

$$|c_m(t')|^2 \cong \frac{\mathcal{E}_0^2}{\hbar^2}|H'_{mn}|^2\frac{\sin^2[(\omega_{mn}-\omega)t'/2]}{[(\omega_{mn}-\omega)]^2} = \frac{\mathcal{E}_0^2}{4\hbar^2}|H'_{mn}|^2\frac{\sin^2[(\omega_{mn}-\omega)t'/2]}{[(\omega_{mn}-\omega)/2]^2}$$

$|c_m(t')|^2$ is the probability that the system is in the state $|m\rangle$ as a consequence of the $n \rightarrow m$ transition. Before we proceed further, let us recall a few things that we have already seen, and think over what we have done so far:

(a) The treatment is able to explain stimulated absorption ($\omega_{mn} = \omega$).
(b) The treatment accounts for stimulated emission ($\omega_{mn} = -\omega$) as well.
(c) The method adopted by us somehow fails to account for the crucial spontaneous emission.
(d) For the treatment done so far, we have considered a plane polarized radiation whose electric field oscillates along the x direction.

Should we **invoke the photon concept**, within our description, and make an attempt to **explain** the phenomenon of **spontaneous emission**? Yes.

To invoke the photon concept of radiation, we will perform certain necessary changes to the relation for the **probability of absorption**, $|c_m(t')|^2$,

$$|c_m(t')|^2 \approx \frac{\mathcal{E}_0^2}{4\hbar^2}|H'_{mn}|^2\frac{\sin^2[(\omega_{mn}-\omega)t'/2]}{[(\omega_{mn}-\omega)/2]^2} = \frac{\mathcal{E}_0^2}{4}\left(\frac{|H'_{mn}|}{\hbar}\right)^2\frac{\sin^2[(\omega_{mn}-\omega)t'/2]}{[(\omega_{mn}-\omega)/2]^2}$$

We recall that, $\omega_{mn} = 2\pi\nu_{mn}$ and $\omega = 2\pi\nu$, so that,

$$\frac{\sin^2[(\omega_{mn}-\omega)t'/2]}{[(\omega_{mn}-\omega)/2]^2} = 4\frac{\sin^2[\pi(\nu_{mn}-\nu)t']}{4\pi^2(\nu_{mn}-\nu)^2}$$

$$\therefore |c_m(t')|^2 \approx \frac{\mathcal{E}_0^2}{4}\left(\frac{|H'_{mn}|}{\hbar}\right)^2 4\frac{\sin^2[\pi(\nu_{mn}-\nu)t']}{4\pi^2(\nu_{mn}-\nu)^2} = \left(\frac{\mathcal{E}_0|H'_{mn}|}{\hbar}\right)^2\frac{\sin^2[\pi(\nu_{mn}-\nu)t']}{4\pi^2(\nu_{mn}-\nu)^2}$$

If $\rho(\nu)$ is the energy density of the radiation field (in units of energy per m^3), it can be shown that,

$$\rho(\nu) = \frac{\epsilon_0}{2}\mathcal{E}_0^2,$$

where, ϵ_0 is the permittivity of free space. However, we note that in our treatment we have considered a radiation that is x-polarized and the direction of propagation is along the z axis. Thus, in our case, the energy density of the radiation field is, $\rho_z(\nu) = \epsilon_0\mathcal{E}_0^2/2$.

Therefore, from,

$$|c_m(t')|^2 \approx \left(\frac{\mathcal{E}_0|H'_{mn}|}{\hbar}\right)^2\frac{\sin^2[\pi(\nu_{mn}-\nu)t']}{4\pi^2(\nu_{mn}-\nu)^2} \text{ and } \rho_z(\nu) = \epsilon_0\mathcal{E}_0^2/2$$

we have,

$$|c_m(t')|^2 \approx \frac{2\,\rho_z(\nu)}{\epsilon_0}\left(\frac{|H'_{mn}|}{\hbar}\right)^2\frac{\sin^2[\pi(\nu_{mn}-\nu)t']}{4\pi^2(\nu_{mn}-\nu)^2}$$

We have just said that we have included a subscript z on the radiation density, to designate that this is the electromagnetic energy density associated with the fraction of the photons moving in the z direction. For a volume in which the distribution of radiation is isotropic, the density associated with light waves propagating forward or backward in any one of the three Cartesian directions is one-third the total radiation density, so that

$$\rho_z(\nu) = \frac{1}{3}\rho(\nu).$$

Therefore, in terms of $\rho(\nu)$, we have,

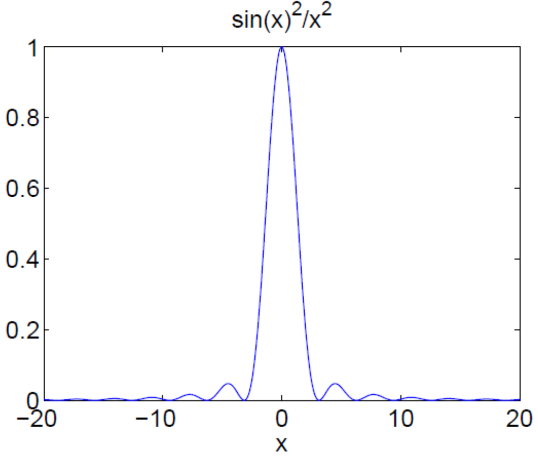
$$|c_m(t')|^2 \approx \frac{2\rho(\nu)|H'_{mn}|^2}{3\epsilon_0\hbar^2}\frac{\sin^2[\pi(\nu_{mn}-\nu)t']}{4\pi^2(\nu_{mn}-\nu)^2}.$$

We now introduce a variable transformation, $x = \pi(\nu_{mn}-\nu)t'$, on

$$|c_m(t')|^2 \approx \frac{2\rho(\nu)|H'_{mn}|^2}{3\epsilon_0\hbar^2}\frac{\sin^2[\pi(\nu_{mn}-\nu)t']}{4\pi^2(\nu_{mn}-\nu)^2},$$

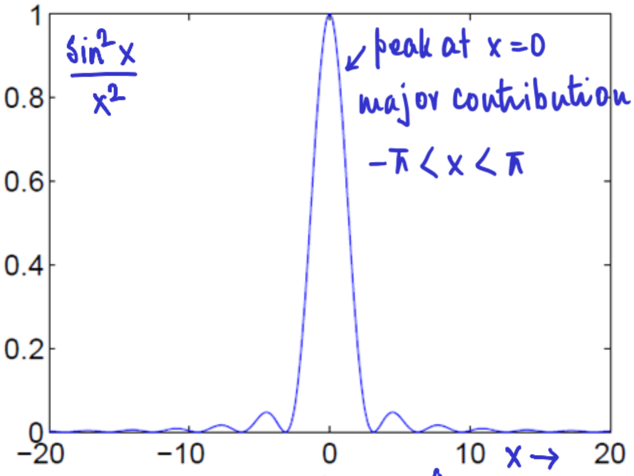
to obtain,

$$|c_m(t')|^2 \approx \frac{t'^2\rho(\nu)|H'_{mn}|^2}{6\epsilon_0\hbar^2}\frac{\sin^2 x}{x^2}.$$



The function is sharply peaked at $x = 0$. The important contribution is limited to $-\pi < x < \pi$. Once t' is larger than $1/|\nu_{mn}-\nu|$, then $|c_m(t')|^2$ will be quite small. At times longer than this limit, only light of frequency $\nu \cong \nu_{mn}$ will make any contribution to transferring population from state n to state m. This leads to the statement, first postulated by Bohr in his model of the H atom, that an atom will undergo a transition from level n to level m only when exposed to frequency of $\nu = (E_m - E_n)/h$. However, at very short times, absorption can occur over a small, but finite, range of frequencies centered about $\nu = \nu_{mn}$. We now integrate the expression for $|c_m(t')|^2$ over all frequencies, and represent it as, $\langle|c_m(t')|^2\rangle$.

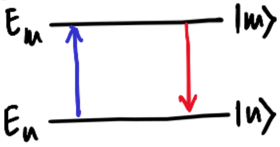
$$\therefore \langle|c_m(t')|^2\rangle = \frac{t'^2|H'_{mn}|^2}{6\epsilon_0\hbar^2}\int_0^\infty \frac{\rho(\nu)\sin^2 x}{x^2}d\nu$$



$$\langle |C_m(t')|^2 \rangle \cong \frac{t'^2 |V_{mn}|^2}{6\epsilon_0 \hbar^2} \int_0^\infty \frac{\rho(\nu)\sin^2 x}{x^2}\, d\nu$$

where, $x = \pi(\nu_{mn} - \nu)t'$

or, $x = \pi\nu_{mn}t' - \pi\nu t'$



$\therefore dx = d(\pi\nu_{mn}t') - d(\pi\nu t')$

or, $dx = 0 - \pi t' d\nu$ or, $dx = -\pi t' d\nu$

$\therefore d\nu = -\frac{1}{\pi t'} dx$

When $\nu \rightarrow 0$, $x \rightarrow \pi\nu_{mn}t'$

When $\nu \rightarrow \infty$, $x \rightarrow -\infty$

$\nu_{mn} = \frac{E_m - E_n}{h}$

$$\therefore \langle |C_m(t')|^2 \rangle = \frac{t'^2 |V_{mn}|^2}{6\epsilon_0 \hbar^2} \int_{\pi\nu_{mn}t'}^{-\infty} \frac{\rho(\nu)\sin^2 x}{x^2} \left(-\frac{1}{\pi t'}\right) dx$$

$$\text{or, } \langle |C_m(t')|^2 \rangle = -\frac{t' |V_{mn}|^2}{6\pi\epsilon_0 \hbar^2} \int_{\pi\nu_{mn}t'}^{-\infty} \frac{\rho(\nu)\sin^2 x}{x^2}\, dx = \frac{t' |V_{mn}|^2}{6\pi\epsilon_0 \hbar^2} \int_{-\infty}^{\pi\nu_{mn}t'} \frac{\rho(\nu)\sin^2 x}{x^2}\, dx$$

$\because \nu_{mn}$ is appreciably large, $\pi\nu_{mn}t' \sim +\infty$ w.r.to $-\infty$

$$\therefore \langle |C_m(t')|^2 \rangle = \frac{t' |V_{mn}|^2}{6\pi\epsilon_0 \hbar^2} \int_{-\infty}^{\infty} \frac{\rho(\nu)\sin^2 x}{x^2}\, dx$$

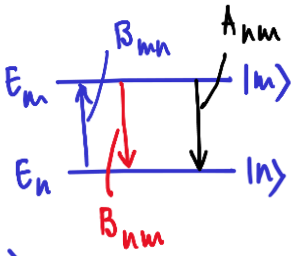
Region	Frequency (Hz)
MW	$10^{11} - 10^{13}$
IR	$10^{13} - 10^{14}$
Near IR	$1\times10^{14} - 4\times10^{14}$
Visible	$4\times10^{14} - 7\frac{1}{2}\times10^{14}$
UV	$10^{15} - 10^{17}$
⋮	

Approximation: photon density remains constant over the range of integration.

$\therefore \rho(\nu) \cong \rho(\nu_{mn})$: not a function of ν; comes out of the integral

$$\therefore \langle |C_m(t')|^2 \rangle = \frac{t' \rho(\nu_{mn}) |V_{mn}|^2}{6\pi\epsilon_0 \hbar^2} \int_{-\infty}^{\infty} \frac{\sin^2 x}{x^2}\, dx \; ; \quad \int_{-\infty}^{\infty} \frac{\sin^2 x}{x^2}\, dx = \pi$$

$$\therefore \langle |C_m(t')|^2 \rangle = \frac{t' \rho(\nu_{mn}) |V_{mn}|^2}{6\epsilon_0 \hbar^2}$$



Say, N_m = population (no. of molecules/atoms) in the state $|m\rangle$

$\frac{dN_m}{dt}$ = rate at which the e.m. radiation populates the state $|m\rangle$

N_n = population in the state $|n\rangle$

$\frac{dN_m}{dt} \propto \rho(\nu_{mn}) N_n \Rightarrow \frac{dN_m}{dt} = \underline{B}_{mn} N_n \rho(\nu_{mn})$: Overall rate of absorption (stimulated)

$\frac{dN_n}{dt} \propto \rho(\nu_{nm}) N_m \Rightarrow \frac{dN_n}{dt} = B_{nm}\, \rho(\nu_{nm}) N_m$: overall rate of stimulated emission

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-20, 20/10/2024)

$B_{mn} = \frac{|V_{mn}|^2}{6\epsilon_0\hbar^2}$ = rate (constant) for stimulated absorption

Equm. statistical mechanics:
no. of molecules in the lower state, $N_n >$ no. of molecules in the upper state, N_m

$\rho(\nu_{nm}) = \rho(\nu_{mn})$

$\frac{N_m}{N_n} = \frac{e^{-h\nu_m/k_BT}}{e^{-h\nu_n/k_BT}}$ or, $N_m/N_n = \exp[-h(\nu_m-\nu_n)/k_BT]$

or, $N_m/N_n = e^{-h\nu_{mn}/k_BT}$

∵ $N_n > N_m$, the overall rate of stimulated absorption > the overall rate of stimulated emission

$\frac{dN_m}{dt} > \frac{dN_n}{dt}$

Spontaneous emission

rate of spontaneous emission, $\left(\frac{dN_n}{dt}\right)_{spon.} = A_{nm}N_m$

Total rate of emission $= \frac{dN_n}{dt} + \left(\frac{dN_n}{dt}\right)_{spon} = N_m\rho(\nu_{nm})B_{nm} + A_{nm}N_m$
$= N_m\left[A_{nm} + B_{nm}\rho(\nu_{nm})\right]$

$$\boxed{N_m\left[A_{nm} + \rho(\nu_{nm})B_{nm}\right] = N_n B_{mn}\rho(\nu_{mn})}$$

or, $N_m\left[A_{n\leftarrow m} + \rho(\nu_{n\leftarrow m})B_{n\leftarrow m}\right] = N_n B_{m\leftarrow n}\rho(\nu_{m\leftarrow n})$

We now integrate the expression for $|c_m(t')|^2$ over all frequencies, and represent it as, $\langle|c_m(t')|^2\rangle$. This will give the total contribution of the radiation field of density $\rho(\nu)$ to population transfer into state m.

$$\langle|c_m(t')|^2\rangle = \frac{t'^2|H'_{mn}|^2}{6\epsilon_0\hbar^2}\int_0^\infty \frac{\rho(\nu)\sin^2 x}{x^2}d\nu$$

We know that, $x = \pi(\nu_{mn}-\nu)t' = \pi\nu_{mn}t' - \pi\nu t'$, so that, $dx = -\pi t' d\nu$.

$$\therefore \langle|c_m(t')|^2\rangle = \frac{t'^2|H'_{mn}|^2}{6\epsilon_0\hbar^2}\int_0^\infty \frac{\rho(\nu)\sin^2 x}{x^2}d\nu = -\frac{t'^2|H'_{mn}|^2}{6\epsilon_0\hbar^2}\int_0^\infty \frac{\rho(\nu)\sin^2 x}{x^2}\frac{1}{\pi t'}dx$$

Note that: When $\nu \to 0,\ x \to \pi\nu_{mn}t'$ and when $\nu \to \infty,\ x \to -\infty$.

$$\text{or, } \langle|c_m(t')|^2\rangle = -\frac{t'|H'_{mn}|^2}{6\pi\epsilon_0\hbar^2}\int_{\pi\nu_{mn}t'}^{-\infty} \frac{\rho(\nu)\sin^2 x}{x^2}dx$$

Thus, we have,

$$\langle|c_m(t')|^2\rangle = -\frac{t'|H'_{mn}|^2}{6\pi\epsilon_0\hbar^2}\int_{\pi\nu_{mn}t'}^{-\infty} \frac{\rho(\nu)\sin^2 x}{x^2}dx$$

Since typical frequencies ν_{mn} are very large, we may replace the lower limit of integration by $+\infty$.

$$\langle|c_m(t')|^2\rangle = -\frac{t'|H'_{mn}|^2}{6\pi\epsilon_0\hbar^2}\int_{+\infty}^{-\infty} \frac{\rho(\nu)\sin^2 x}{x^2}dx = \frac{t'|H'_{mn}|^2}{6\pi\epsilon_0\hbar^2}\int_{-\infty}^{+\infty} \frac{\rho(\nu)\sin^2 x}{x^2}dx$$

We further assume that the photon density is constant over the range sampled by the integral, so that, $\rho(\nu) \approx \rho(\nu = \nu_{mn}) = \rho(\nu_{mn})$, then, we can take the density out from the integral, to get

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-20, 20/10/2024)

$$\langle |c_m(t')|^2\rangle = \frac{t'\rho(\nu_{mn})|H'_{mn}|^2}{6\pi\epsilon_0\hbar^2}\int_{-\infty}^{+\infty}\frac{\sin^2 x}{x^2}dx = \frac{t'\rho(\nu_{mn})|H'_{mn}|^2}{6\pi\epsilon_0\hbar^2}\times\pi$$

so that,

$$\langle |c_m(t')|^2\rangle = \frac{t'\rho(\nu_{mn})|H'_{mn}|^2}{6\epsilon_0\hbar^2},\ \text{since,}\ \int_{-\infty}^{+\infty}\frac{\sin^2 x}{x^2}dx = \pi$$

Thus, we have,

$$\langle |c_m(t')|^2\rangle = \frac{t'\rho(\nu_{mn})|H'_{mn}|^2}{6\epsilon_0\hbar^2}.$$

The derivative of the population in state m with respect to time is the rate at which the light field populates level m starting with the system in level n. This rate is proportional to the radiation density at frequency $\nu = \nu_{mn}$. The constant of proportionality, called the **Einstein B coefficient**, is

$$B_{mn} = \frac{|H'_{mn}|^2}{6\epsilon_0\hbar^2}.$$

If level m lies higher than level n, then this B coefficient is the rate for stimulated absorption (absorption of energy stimulated by the electromagnetic field). It is proportional to the square of the matrix element of the dipole operator between states n and m. Since the absolute value squared of the matrix element of any physical operator is independent of the order of the initial and final states, it is also clear that the rate of stimulated absorption (level n to level m) is identical to the rate of stimulated emission (level m to level n). Let the total number of molecules in levels n and m be N_n and N_m. The overall rate of stimulated absorption (energy absorbed per unit time) is

$$N_n\rho(\nu_{mn})B_{mn}$$

while the overall rate of stimulated emission (energy emitted per unit time) is

$$N_m\rho(\nu_{nm})B_{nm}$$

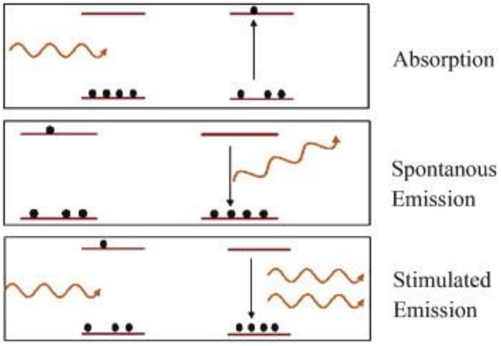
Obviously, $\rho(\nu_{mn}) = \rho(\nu_{nm})$. However, equilibrium statistical mechanics demonstrates that the number of molecules in the lower state must be larger than the number in a higher state. Specifically, at equilibrium

$$N_m/N_n = \exp(-h\nu_{mn}/k_B T).$$

Since the number of molecules in the lower energy state is greater, the overall rate of stimulated absorption will be greater than the overall rate of stimulated emission, so that, eventually, the number of molecules in the two states will equilibrate, which is contrary to the predictions of equilibrium statistical mechanics. To resolve this paradox, Einstein proposed the existence of another process, **spontaneous emission**. He postulated that **there exists a small probability for an excited molecule (or atom) to release a photon even in the absence of an electromagnetic field**. The rate of spontaneous emission, which is denoted A_{nm}, will be thus independent of the energy density of the radiation field. Therefore, the total rate of energy emission from the upper state is $N_m\rho(\nu_{nm})B_{nm} + A_{nm}N_m = N_m[A_{nm} + \rho(\nu_{nm})B_{nm}]$. This must be equal to the overall rate of energy absorption from the lower state, given by

$$N_n\rho(\nu_{mn})B_{mn},$$

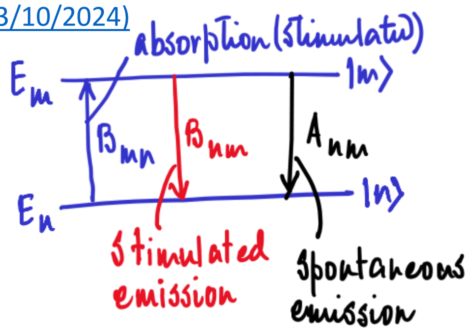
that is, $N_m[A_{nm} + \rho(\nu_{nm})B_{nm}] = N_n\rho(\nu_{mn})B_{mn}$, where we make the notations to make them even more explicit (to avoid any confusion), and express as, $N_m[A_{n\leftarrow m} + \rho(\nu_{n\leftarrow m})B_{n\leftarrow m}] = N_n\rho(\nu_{m\leftarrow n})B_{m\leftarrow n}$. The system we are dealing with is essentially a two-level system with the ground state E_n and an excited state E_m. $E_m - E_n \gg k_B T \Rightarrow$ thermal energy is insufficient for a $n \to m$ transition.



GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-21, 23/10/2024)

$$N_m\left[A_{nm}+\rho(\nu_{nm})B_{nm}\right]=N_nB_{mn}\rho(\nu_{mn})$$

or, equivalently, $N_m\left[A_{n\leftarrow m}+\rho(\nu_{n\leftarrow m})B_{n\leftarrow m}\right]$
$= N_n\left[B_{m\leftarrow n}\,\rho(\nu_{m\leftarrow n})\right]$



$$B_{mn}=|V_{mn}|^2/6\epsilon_0\hbar^2$$

$$\boxed{\text{What are the units/dimensions of } A_{nm},\ B_{nm} \text{ and } B_{mn}?}$$

Rate of spontaneous emission, $-\dfrac{dN_m(t)}{dt}=A_{nm}N_m(t)$

$$A_{nm}=-\left(\frac{1}{N_m(t)}\right)\left(\frac{dN_m(t)}{dt}\right)$$

Spontaneous emission behaves like a first-order process.

$$\text{number}^{-1}\times\text{number}\cdot\text{second}^{-1}=\text{second}^{-1}$$

Rate of stimulated emission, $-\dfrac{dN_m(t)}{dt}=B_{nm}\rho(\nu_{nm})N_m(t)$

$$\therefore B_{nm}=-\frac{1}{\rho(\nu_{nm})N_m(t)}\frac{dN_m(t)}{dt}\rightarrow\frac{1}{J\,m^{-3}\,s\times\text{number}}\cdot\frac{\text{number}}{s}=J^{-1}m^3\,s^{-2}$$

$$\rightarrow N^{-1}m^{-1}m^3\,s^{-2}=(kg\,m\,s^{-2})^{-1}m^{-1}m^3\,s^{-2}=m\,kg^{-1}$$

Rate of absorption, $B_{mn}\rightarrow m\,kg^{-1}$

$$\boxed{\text{How are } A_{nm},\ B_{nm} \text{ and } B_{mn} \text{ related to each other?}}$$

at thermal eqm. N_n and N_m do not evolve in time: $-\dfrac{dN_n(t)}{dt}=0,\ \dfrac{dN_m(t)}{dt}=0$

$\rho(\nu_{nm})=\rho(\nu_{mn})=\rho(\nu)=$ eqm. value of the spectral radiant energy density.

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

Under the condition of thermal eqm. $N_m\left[A_{nm}+\rho(\nu_{nm})B_{nm}\right]=N_n\rho(\nu_{mn})B_{mn}$

or, $N_m\left[A_{nm}+\rho(\nu)B_{nm}\right]=N_n\,\rho(\nu)B_{mn}$

or, $N_mA_{nm}=\rho(\nu)\left[N_nB_{mn}-N_mB_{nm}\right]$ or, $\rho(\nu)=\dfrac{N_mA_{nm}}{N_nB_{mn}-N_mB_{nm}}$

or, $\rho(\nu)=\dfrac{A_{nm}}{(N_n/N_m)B_{mn}-B_{nm}}$

From Boltzmann distribution, at thermal eqm. $\dfrac{N_n}{N_m}=e^{h\nu/k_BT}$

$$\therefore \rho(\nu)=\frac{A_{nm}}{B_{mn}e^{h\nu/k_BT}-B_{nm}},\quad \rho(\nu)=\frac{8\pi h}{c^3}\frac{\nu^3}{e^{h\nu/k_BT}-1}$$

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-21, 23/10/2024)

For the two relations to hold simultaneously, $B_{nm} = B_{mn} = B$

$$A = A_{nm} = \frac{8\pi h\nu^3}{c^3} B \quad , \quad B = \frac{|V_{mn}|^2}{6\epsilon_0\hbar^2}$$

$$A = \frac{8\pi h\nu^3}{c^3}\,\frac{|V_{mn}|^2}{6\epsilon_0\hbar^2}$$

Selection rules

① particle of charge q in a 1D box

$$\langle\psi_m|\hat{\mu}_x|\psi_n\rangle = q\int_0^L \left(\frac{2}{L}\right) x \sin\left(\frac{m\pi x}{L}\right)\sin\left(\frac{n\pi x}{L}\right)dx$$

$$\hat{\mu}_x = q\hat{x}$$

$$\int x\sin(ax)\sin(bx)\,dx = \frac{\cos[(a-b)x]}{2(a-b)^2} - \frac{\cos[(a+b)x]}{2(a+b)^2} + \frac{x\sin[(a-b)x]}{2(a-b)} - \frac{x\sin[(a+b)x]}{2(a+b)} + C$$

$$\langle\psi_m|\hat{\mu}_x|\psi_n\rangle = \frac{qL}{\pi^2}\left[\underbrace{\frac{1}{(m-n)^2}\left[(-1)^{m-n}-1\right]}_{\text{to be} \neq 0,\ m-n \text{ must be an odd no.}} - \underbrace{\frac{1}{(m+n)^2}\left[(-1)^{m+n}-1\right]}_{\text{to be} \neq 0,\ m+n \text{ must be an odd no.}}\right]$$

② a particle of charge q moving in a 1D SHO potential.

$$\hat{x} = \left(\frac{\hbar}{2m\omega}\right)^{1/2}(a+a^\dagger) \qquad \langle m|\hat{x}|n\rangle = \langle m|a+a^\dagger|n\rangle = \langle m|a|n\rangle + \langle m|a^\dagger|n\rangle$$

$$= \sqrt{n}\,\langle m|n-1\rangle + \sqrt{n+1}\,\langle m|n+1\rangle$$

SHO eigenfunctions are orthonormal, $\langle\alpha|\beta\rangle = \delta_{\alpha\beta}$

$m = n-1$ or, $m-n = -1$

$m = n+1$ or, $m-n = +1$

$$\therefore \Delta\nu = \pm 1$$

What are the units of Einstein A and B coefficients? Rate of spontaneous emission,

$$-\frac{dN_m(t)}{dt} = A_{n\leftarrow m}N_m(t)$$

so that,

$$A_{n\leftarrow m} = -\left(\frac{1}{N_m(t)}\right)\left(\frac{dN_m(t)}{dt}\right) \rightsquigarrow \text{number}^{-1}\times\text{number}\cdot\text{second}^{-1} = \text{s}^{-1}.$$

Thus, spontaneous emission behaves like a first-order process. Similarly, for the stimulated emission, the rate equation is,

$$-\frac{dN_m(t)}{dt} = B_{n\leftarrow m}\rho(\nu_{n\leftarrow m})N_m(t) \Rightarrow B_{n\leftarrow m} = -\left(\frac{1}{\rho(\nu_{n\leftarrow m})N_m(t)}\right)\left(\frac{dN_m(t)}{dt}\right)$$

$$\rightsquigarrow \left(\frac{1}{\text{J}\cdot\text{m}^{-3}\cdot\text{second}\times\text{number}}\right)\left(\frac{\text{number}}{\text{second}}\right) = \text{J}^{-1}\text{m}^3\text{s}^{-2} = \text{N}^{-1}\text{m}^{-1}\text{m}^3\text{s}^{-2}$$

$$= (\text{kg m s}^{-2})^{-1}\text{m}^{-1}\text{m}^3\text{s}^{-2} = \text{m kg}^{-1}.$$

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-21, 23/10/2024)

In the same manner, $B_{m\leftarrow n} \rightsquigarrow \mathrm{m\,kg^{-1}}$. How are the three Einstein coefficients, $B_{n\leftarrow m}$, $A_{n\leftarrow m}$ and $B_{m\leftarrow n}$ related? A relationship between these three can be determined in the limit at which the states E_n and E_m are in thermal equilibrium, in which case neither N_n, nor N_m evolve/vary in time.

$$-\frac{dN_n(t)}{dt} = \frac{dN_m(t)}{dt} = 0$$

and $\rho(\nu_{m\leftarrow n}) = \rho(\nu_{n\leftarrow m}) = \rho(\nu)$ is the equilibrium spectral radiant energy density. We can assume that $\rho(\nu)$ comes from a thermal blackbody radiation source. Therefore,

$$\rho(\nu) = \frac{8\pi h}{c^3}\frac{\nu^3}{e^{h\nu/k_B T} - 1}$$

Under the condition of thermal equilibrium,

$$N_m[A_{n\leftarrow m} + \rho(\nu_{n\leftarrow m})B_{n\leftarrow m}] = N_n\rho(\nu_{m\leftarrow n})B_{m\leftarrow n},$$

that is,

$$N_m[A_{n\leftarrow m} + \rho(\nu)B_{n\leftarrow m}] = N_n\rho(\nu)B_{m\leftarrow n} \Rightarrow N_m A_{n\leftarrow m} = \rho(\nu)[N_n B_{m\leftarrow n} - N_m B_{n\leftarrow m}],$$

so that,

$$\rho(\nu) = \frac{N_m A_{n\leftarrow m}}{N_n B_{m\leftarrow n} - N_m B_{n\leftarrow m}} \Rightarrow \rho(\nu) = \frac{A_{n\leftarrow m}}{(N_n/N_m)B_{m\leftarrow n} - B_{n\leftarrow m}}$$

From Boltzmann distribution (for a system in equilibrium at temperature T), we have,

$$\frac{N_m}{N_n} = e^{-(E_m - E_n)/k_B T} = e^{-h\nu/k_B T} \Rightarrow \frac{N_n}{N_m} = e^{h\nu/k_B T}$$

$$\therefore \rho(\nu) = \frac{A_{n\leftarrow m}}{B_{m\leftarrow n}e^{h\nu/k_B T} - B_{n\leftarrow m}}$$

The only way that,

$$\rho(\nu) = \frac{8\pi h}{c^3}\frac{\nu^3}{e^{h\nu/k_B T} - 1} \text{ and } \rho(\nu) = \frac{A_{n\leftarrow m}}{B_{m\leftarrow n}e^{h\nu/k_B T} - B_{n\leftarrow m}}$$

is to have, $B_{m\leftarrow n} = B_{n\leftarrow m} = B$ and

$$A = A_{n\leftarrow m} = \frac{8\pi h\nu^3}{c^3}B$$

Note that, the A coefficient depends on the cube of the frequency. Spontaneous emission is much more probable for ultraviolet transitions than for microwave transitions.

It can be shown that,

- the two-level system is unable to achieve a population inversion, while
- for a three-level system a population inversion can be true.

We will return to these issues when we discuss the LASERs. Therefore, we conclude that for any transition from an initial (i) to a final (f) state, we have,

$$B_{mn} = \frac{|H'_{mn}|^2}{6\epsilon_0\hbar^2} \quad \text{and} \quad A_{mn} = \frac{8\pi h\nu_{mn}^3}{c^3}B_{mn} \quad (\text{with } B_{mn} = B_{nm})$$

Selection Rules: Transitions Within the Same Electronic State

Both the Einstein A and B coefficients depend on the square of the matrix element of the dipole-moment operator. The dipole-moment operator, $\hat{\mu}_x$, as defined earlier, is used to calculate the transition dipole integral, $\langle\psi_m|\hat{\mu}_x|\psi_n\rangle$.

Case-1: Electric-dipole selection rules for a particle of charge q in a one-dimensional box.

$$\langle\psi_m|\hat{\mu}_x|\psi_n\rangle = q\int_0^L \left(\frac{2}{L}\right)x\sin\left(\frac{m\pi x}{L}\right)\sin\left(\frac{n\pi x}{L}\right)dx$$

Note that:

$$\int x\sin(ax)\sin(bx)\,dx = \frac{\cos[(a-b)x]}{2(a-b)^2} - \frac{\cos[(a+b)x]}{2(a+b)^2} + \frac{x\sin[(a-b)x]}{2(a-b)^2} - \frac{x\sin[(a+b)x]}{2(a+b)^2}$$

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-21, 23/10/2024)

$$\therefore \langle\psi_m|\hat{\mu}_x|\psi_n\rangle = \frac{2q}{L}\left[\begin{aligned} &\frac{\cos[(m-n)\pi x/L]}{2(m-n)^2\pi^2/L^2} - \frac{\cos[(m+n)\pi x/L]}{2(m+n)^2\pi^2/L^2} \\ &+ \frac{x\sin[(m-n)\pi x/L]}{2(m-n)^2\pi^2/L^2} - \frac{x\sin[(m+n)\pi x/L]}{2(m+n)^2\pi^2/L^2} \end{aligned}\right]$$

Therefore,

$$\langle\psi_m|\hat{\mu}_x|\psi_n\rangle = 2qL\left[\begin{aligned} &\left.\frac{\cos[(m-n)\pi x/L]}{2(m-n)^2\pi^2}\right|_0^L - \left.\frac{\cos[(m+n)\pi x/L]}{2(m+n)^2\pi^2}\right|_0^L \\ &+ \left.\frac{x\sin[(m-n)\pi x/L]}{2(m-n)^2\pi^2}\right|_0^L - \left.\frac{x\sin[(m+n)\pi x/L]}{2(m+n)^2\pi^2}\right|_0^L \end{aligned}\right]$$

$$\langle\psi_m|\hat{\mu}_x|\psi_n\rangle = 2qL\left[\begin{aligned} &\frac{1}{2(m-n)^2\pi^2}\{\cos(m-n)\pi - 1 + x\sin(m-n)\pi - 0\} \\ &- \frac{1}{2(m+n)^2\pi^2}\{\cos(m+n)\pi - 1 + x\sin(m+n)\pi - 0\} \end{aligned}\right]$$

Note that, all sine terms are zero, irrespective of the values of m and n.

$$\therefore \langle\psi_m|\hat{\mu}_x|\psi_n\rangle = \frac{qL}{\pi^2}\left[\frac{1}{(m-n)^2}\{\cos(m-n)\pi - 1\} - \frac{1}{(m+n)^2}\{\cos(m+n)\pi - 1\}\right]$$

$$\text{or, } \langle\psi_m|\hat{\mu}_x|\psi_n\rangle = \frac{qL}{\pi^2}\left[\frac{1}{(m-n)^2}\left\{(-1)^{(m-n)} - 1\right\} - \frac{1}{(m+n)^2}\left\{(-1)^{(m+n)} - 1\right\}\right]$$

Thus,

$$\langle\psi_m|\hat{\mu}_x|\psi_n\rangle = \frac{qL}{\pi^2}\left[\frac{1}{(m-n)^2}\left\{(-1)^{(m-n)} - 1\right\} - \frac{1}{(m+n)^2}\left\{(-1)^{(m+n)} - 1\right\}\right]$$

The first term in the square bracket is non-zero only if $(m-n)$ is odd; the second term is non-vanishing provided $(m+n)$ is odd. These determine the rules for the spectroscopic transitions for the system.

Case-2: Electric-dipole selection rules for a one-dimensional harmonic oscillator of charge q. We must find out $q\langle m|\hat{x}|n\rangle$. We recall that,

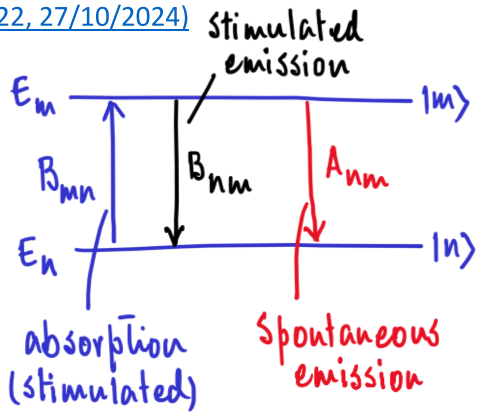
$$\hat{x} = \left(\frac{\hbar}{2m\omega}\right)^{1/2}(a + a^\dagger),$$

so that,

$$\langle m|\hat{x}|n\rangle = \langle m|a + a^\dagger|n\rangle = \langle m|a|n\rangle + \langle m|a^\dagger|n\rangle = \sqrt{n}\langle m|n-1\rangle + \sqrt{n+1}\langle m|n+1\rangle$$

Since, SHO eigenfunctions are orthonormal, either $m = n - 1$, or $m = n + 1$, that is, $m - n = \pm 1$. Therefore, for the 1D SHO, the selection rule will be, $\Delta v = \pm 1$.

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-22, 27/10/2024)



$B_{mn} = \frac{|V_{mn}|^2}{6\epsilon_0\hbar^2}$, $B_{mn} = B_{nm} = B$

$A_{nm} = A = \frac{8\pi h\nu^3}{c^3} B$, or, $A = \frac{8\pi h\nu^3}{c^3}\frac{|V_{mn}|^2}{6\epsilon_0\hbar^2}$

LASER: Light Amplification by Stimulated Emission of Radiation.

increase/enhancement of intensity

$|m\rangle$ to $|n\rangle$ prob. > $|n\rangle$ to $|m\rangle$ prob.

Rate of stimulated emission, $-\frac{dN_m(t)}{dt} = \boxed{B_{nm}\rho(\nu_{nm})N_m(t)}$

Rate of absorption (stimulated), $-\frac{dN_n(t)}{dt} = \frac{dN_m(t)}{dt} = B_{mn}\rho(\nu_{mn})N_n(t)$

∴ For LASER action, $B_{nm}\rho(\nu_{nm})N_m(t) > B_{mn}\rho(\nu_{mn})N_n(t)$

Now, $B_{nm} = B_{mn} = B$, $A_{nm} = A$, and $\rho(\nu_{nm}) = \rho(\nu_{mn}) = \rho(\nu)$

$B\rho(\nu)N_m(t) > B\rho(\nu)N_n(t) \Rightarrow \boxed{N_m(t) > N_n(t)}$: population inversion

∴ for LASER action, there must be a population inversion.

Boltzmann distribution, at any temp. T, $\frac{N_m(t)}{N_n(t)} = e^{-(E_m-E_n)/k_BT}$ (equ. thermal dist.)

∵ $(E_m-E_n)/k_BT > 0$ (always) $\Rightarrow N_m(t)/N_n(t) < 1 \Rightarrow \boxed{N_m(t) < N_n(t)}$

⇒ $\boxed{\text{population inversion is a non-equilibrium situation}}$

Overall rate equation for the non-degenerate two-level system

$$-\frac{dN_n(t)}{dt} = \frac{dN_m(t)}{dt} = B_{mn}\rho(\nu_{mn})N_n(t) - A_{nm}N_m(t) - B_{nm}\rho(\nu_{nm})N_m(t)$$

or, $\frac{dN_m(t)}{dt} = B\rho(\nu)\left[N_n(t) - N_m(t)\right] - AN_m(t)$

$N_{total} = N_n(t) + N_m(t)$, N_{total} is a constant of time for a closed system.

$N_n(t) = N_{total} - N_m(t)$; when $t=0$, $N_n(0) = N_{total}$, $N_m(0) = 0$

∴ $\frac{dN_m(t)}{dt} = B\rho(\nu)\left[N_{total} - 2N_m(t)\right] - AN_m(t)$

or, $\frac{dN_m(t)}{dt} = B\rho(\nu)N_{total} - [A+2B\rho(\nu)]N_m(t)$

Say, $\alpha = B\rho(\nu)N_{total}$
$\beta = A+2B\rho(\nu)$

or, $dt = \frac{dN_m(t)}{B\rho(\nu)N_{total} - [A+2B\rho(\nu)]N_m(t)}$

∴ $dt = \frac{dN_m(t)}{\alpha - \beta N_m(t)}$ Say, $u = \alpha - \beta N_m(t)$ $\Rightarrow du = -\beta\, dN_m(t)$ ∴ $dN_m(t) = -\frac{1}{\beta}du$

∴ $dt = -\frac{1}{\beta}\frac{du}{u}$ or, $\ln u = -\beta t$ or, $u = e^{-\beta t}$

or, $\alpha - \beta N_m(t) = e^{-\beta t}$ ∴ $N_m(t) = \frac{\alpha}{\beta} - \frac{e^{-\beta t}}{\beta}$

or, $N_m(t) = \frac{\alpha}{\beta}\left[1 - \frac{e^{-\beta t}}{\alpha}\right]$ or, $N_m(t) = \frac{B\rho(\nu)N_{total}}{A+2B\rho(\nu)}\left[1 - \frac{e^{-[A+2B\rho(\nu)]t}}{B\rho(\nu)N_{total}}\right]$

∴ $\frac{N_m(t)}{N_{total}} = \frac{B\rho(\nu)}{A+2B\rho(\nu)}\left[1 - \frac{e^{-[A+2B\rho(\nu)]t}}{B\rho(\nu)N_{total}}\right]$

When $t \to \infty$, $e^{-[A+2B\rho(\nu)]t} \to 0$, $\frac{N_m(\infty)}{N_{total}} = \frac{B\rho(\nu)}{A+2B\rho(\nu)}$

Now, if $A = 0$, i.e. there is no spontaneous emission, $\frac{N_m(\infty)}{N_{total}} = \frac{1}{2}$

$A>0$, almost always: $A+2B\rho(\nu) > B\rho(\nu)$

$\frac{N_m(t)}{N_{total}} < \frac{1}{2}$ or, $\frac{N_m(t)}{N_n(t)+N_m(t)} < \frac{1}{2}$ or, $\frac{1}{\frac{N_n(t)}{N_m(t)}+1} < \frac{1}{2}$

∴ $\frac{N_n(t)}{N_m(t)} > 1$ ⇒ there can be no population inversion for a two-level non-degenerate system

∴ No two-level system can demonstrate LASER action.

Once the source of electromagnetic radiation is switched off $\equiv \rho(\nu) = 0$

$\frac{dN_m(t)}{dt} = B\rho(\nu)[N_n(t) - N_m(t)] - AN_m(t) \Rightarrow \frac{dN_m(t)}{dt} = -AN_m(t)$

$A \to \text{time}^{-1}$
$\boxed{\frac{1}{A}} \to$ time
→ radiative lifetime τ_R

or, $\frac{dN_m(t)}{N_m(t)} = -A\,dt$ or, $\int_{N_m(0)}^{N_m(t)} \frac{dN_m(t)}{N_m(t)} = -A\int_0^t dt$ ∴ $N_m(t) = N_m(0)e^{-At}$

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-22, 27/10/2024)

LASERs are designed to amplify light by the stimulated emission of radiation. For this amplification to occur, a photon that passes through the sample of atoms must have a greater probability of stimulating emission from an electronically excited atom than of being absorbed by an atom in its ground state. This condition requires that the rate of stimulated emission be greater than the rate of absorption, or from

$$-\frac{dN_m(t)}{dt} = B_{nm}\rho(\nu_{nm})N_m(t)\ \text{(stimulated emission only)}$$

and

$$-\frac{dN_n(t)}{dt} = \frac{dN_m(t)}{dt} = B_{mn}\rho(\nu_{mn})N_n(t)\ \text{(absorption only)},$$

we should have,

$$B_{nm}\rho(\nu_{nm})N_m(t) > B_{mn}\rho(\nu_{mn})N_n(t).$$

Now, since, $B_{nm} = B_{mn} = B$, $A_{nm} = A$, and $\rho(\nu_{nm}) = \rho(\nu_{mn}) = \rho(\nu)$, the stimulated emission can be more probable than absorption only when, $N_m(t) > N_n(t)$, or when the population of the excited state is greater than that of the lower state. Such a situation is called **population inversion**. Now, from,

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

N_m must be less than N_n, because $h\nu_{nm}/k_BT$ is a positive quantity. Therefore, a population inversion, for which, $N_m(t) > N_n(t)$, is a non-equilibrium situation. Thus, before we can expect light amplification, a population inversion between the upper and lower levels must be generated. Can we achieve a population inversion for a two-level system? The rate equation for a non-degenerate two-level system is given by,

$$-\frac{dN_n(t)}{dt} = \frac{dN_m(t)}{dt} = B\rho(\nu)N_n(t) - AN_m(t) - B\rho(\nu)N_m(t)$$

$$\text{or,} -\frac{dN_n(t)}{dt} = \frac{dN_m(t)}{dt} = B\rho(\nu)[N_n(t) - N_m(t)] - AN_m(t)$$

Say, $N_{total} = N_n(t) + N_m(t)$, is the total number of particles in the system, which remains constant for a closed system. We note that $N_n(t)$ and $N_m(t)$ vary with time to keep N_{total} a constant of time. If we assume that all the atoms are in the ground state at time $t = 0$, so that $N_n(0) = N_{total}$ and $N_m(0) = 0$, so that, from

$$\frac{dN_m(t)}{dt} = B\rho(\nu)[N_n(t) - N_m(t)] - AN_m(t)$$

we will have, upon substituting $N_n(t) = N_{total} - N_m(t)$,

$$\frac{dN_m(t)}{dt} = B\rho(\nu)[N_{total} - N_m(t) - N_m(t)] - AN_m(t) = B\rho(\nu)[N_{total} - 2N_m(t)] - AN_m(t)$$

$$\text{or,} \frac{dN_m(t)}{dt} = B\rho(\nu)N_{total} - 2B\rho(\nu)N_m(t) - AN_m(t) = B\rho(\nu)N_{total} - [2B\rho(\nu) + A]N_m(t)$$

$$\text{or,} dt = \frac{dN_m(t)}{B\rho(\nu)N_{total} - [A + 2B\rho(\nu)]N_m(t)}$$

For simplicity, let us substitute $\alpha = B\rho(\nu)N_{total}$ and $\beta = A + 2B\rho(\nu)$.

$$\therefore dt = \frac{dN_m(t)}{\alpha - \beta N_m(t)}$$

Now, say, $u = \alpha - \beta N_m(t)$, so that, $du = -\beta dN_m(t) \Rightarrow dN_m(t) = -(1/\beta)du$

$$dt = -\frac{1}{\beta}\frac{du}{u}$$

Integrating both sides of the equation, we get $\ln u = -\beta t$.

$$\therefore u = e^{-\beta t} \Rightarrow \alpha - \beta N_m(t) = e^{-\beta t} \Rightarrow N_m(t) = \frac{\alpha}{\beta} - \frac{1}{\beta}e^{-\beta t} \Rightarrow N_m(t) = \frac{\alpha}{\beta}\left(1 - \frac{e^{-\beta t}}{\alpha}\right)$$

$$\therefore N_m(t) = \frac{B\rho(\nu)N_{total}}{A + 2B\rho(\nu)}\left[1 - \frac{e^{-[2B\rho(\nu)+A]t}}{B\rho(\nu)N_{total}}\right] \Rightarrow \frac{N_m(t)}{N_{total}} = \frac{B\rho(\nu)}{A + 2B\rho(\nu)}\left[1 - \frac{e^{-[2B\rho(\nu)+A]t}}{B\rho(\nu)N_{total}}\right]$$

When $t \to \infty$, $e^{-[A+2B\rho(\nu)]t} \to 0$, so that

$$\frac{N_m(\infty)}{N_{total}} = \frac{B\rho(\nu)}{A + 2B\rho(\nu)}$$

Now, if $A = 0$, there is no spontaneous emission. Hence,

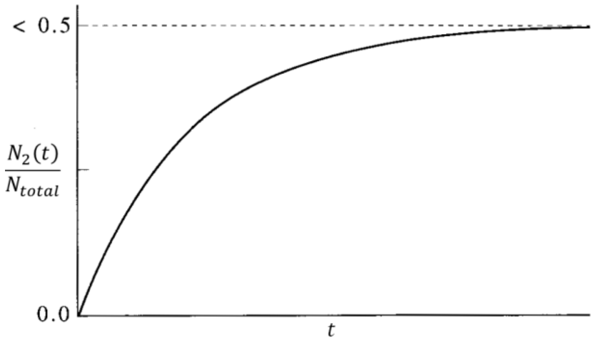
$$\frac{N_m(\infty)}{N_{total}} = \frac{1}{2}$$

However, $A > 0$, always, so that $A + 2B\rho(\nu) > B\rho(\nu)$, and hence

$$\frac{N_m(t)}{N_{total}} < \frac{1}{2} \Rightarrow \frac{N_m(t)}{N_n(t) + N_m(t)} < \frac{1}{2} \Rightarrow \frac{1}{\frac{N_n(t)}{N_m(t)} + 1} < \frac{1}{2}$$

$$\therefore \frac{N_n(t)}{N_m(t)} > 1 \Rightarrow \frac{N_m(t)}{N_n(t)} < 1$$

So, the number of atoms in the excited state can never exceed the number of atoms in the ground state. Thus, a population inversion cannot occur in a two-level system.



How does the system relax back to equilibrium once the incident light source is turned off? Once the light source is turned off, the only pathway by which an excited atom can return to its ground state is by spontaneous emission. Since under such a situation, $\rho(\nu) = 0$, the rate equation,

$$\frac{dN_m(t)}{dt} = B\rho(\nu)[N_n(t) - N_m(t)] - AN_m(t)$$

becomes

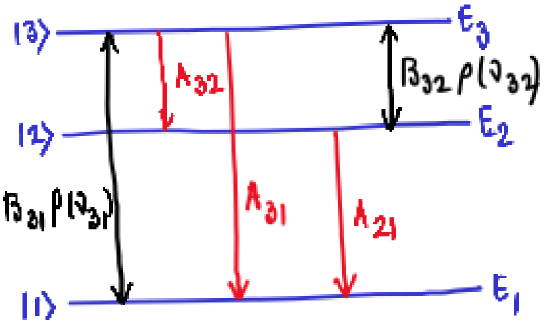
$$\frac{dN_m(t)}{dt} = -AN_m(t),$$

which, upon integration, gives,

$$N_m(t) = N_m(0)e^{-At}.$$

The reciprocal of A is denoted by τ_R and is called the fluorescence lifetime or the radiative lifetime. We will see, that a three-level system can undergo a population inversion and demonstrate lasing.

A Three-level System



* pump light of frequency $\nu_{31} = \frac{E_3 - E_1}{h}$ excites an atom/a molecule from $|1\rangle$ to $|3\rangle$.

* If a light of frequency ν_{31} is incident on the system

(a) absorption from $|1\rangle$ to $|3\rangle$, leading to the populating of $|3\rangle$: $B_{31}\rho(\nu_{31})$

(b) spontaneous emission to $|2\rangle$: A_{32}

(c) " " " $|1\rangle$: A_{31}

(d) stimulated emission to $|1\rangle$: $B_{31}\rho(\nu_{31})$

* Any $B_{ij} = B_{ji}$

* all atoms are in the ground state initially ($t=0$) : $N_1(0) = N_{total}$

* pump freq. ν_{31} does not excite from $|1\rangle$ to $|2\rangle$

* If a light of frequency $\nu_{32} = \frac{E_3 - E_2}{h}$ is incident on the system

$$\left.\begin{array}{l}\text{(a) absorption from } |2\rangle \text{ to } |3\rangle. \\ \text{(b) stimulated emission from } |3\rangle \text{ to } |2\rangle.\end{array}\right\} B_{32}\rho(\nu_{32})$$

$$\boxed{N_{total} = N_1(t) + N_2(t) + N_3(t)}$$

* Rate equations:

$$\frac{dN_1}{dt} = -B_{31}\rho(\nu_{31})N_1 + B_{31}\rho(\nu_{31})N_3 + A_{31}N_3 + A_{21}N_2 \quad \text{—— ①}$$

$$\frac{dN_2}{dt} = A_{32}N_3 - A_{21}N_2 + B_{32}\rho(\nu_{32})N_3 - B_{32}\rho(\nu_{32})N_2 \quad \text{—— ②}$$

$$\frac{dN_3}{dt} = B_{31}\rho(\nu_{31})N_1 - B_{31}\rho(\nu_{31})N_3 - A_{32}N_3 - A_{31}N_3 - B_{32}\rho(\nu_{32})N_3 + B_{32}\rho(\nu_{32})N_2 \quad \text{—— ③}$$

* all the states are non-degenerate; the rate equations apply to the population of states

* at thermal eqm., the populations of all the states are constants of time

$$\therefore \frac{dN_1}{dt} = 0, \frac{dN_2}{dt} = 0, \frac{dN_3}{dt} = 0$$

* from ②: $A_{32}N_3 - A_{21}N_2 + B_{32}\rho(\nu_{32})N_3 - B_{32}\rho(\nu_{32})N_2 = 0$

or, $[A_{32} + B_{32}\rho(\nu_{32})]N_3 = [A_{21} + B_{32}\rho(\nu_{32})]N_2$

or, $\frac{N_3}{N_2} = \frac{A_{21} + B_{32}\rho(\nu_{32})}{A_{32} + B_{32}\rho(\nu_{32})}$ $\therefore N_3 > N_2$ (population inversion) if $A_{21} > A_{32}$

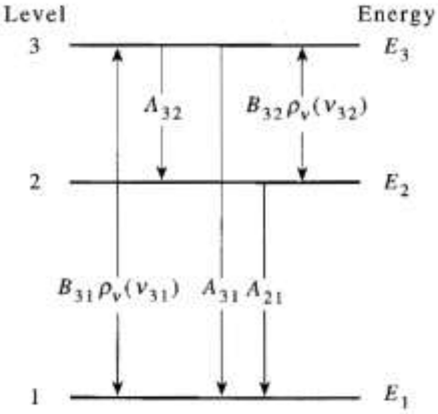
$\therefore$ a population inversion is possible between states $|2\rangle$ and $|3\rangle$ when the atoms excited to state $|3\rangle$ decay relatively slowly to state $|2\rangle$ and those in state $|2\rangle$ decay rapidly back to the ground state, $|1\rangle$.

Such a system is called a gain medium.

GOOGLE MEET LINK: https://meet.google.com/crp-bhxx-vmv (CLASS-23, 10/11/2024)

A Three-Level System

Each level is once again assumed to be non-degenerate and therefore represents a single state of the system. Pump light of frequency given by $h\nu_{31} = E_3 - E_1$ excites an atom from the ground state (state 1) to state 3. Once populated, this excited state can relax by spontaneous emission to states 2 or 1 or by stimulated emission back to the ground state.



Those excited-state atoms that relax by spontaneous emission to state 2 will also undergo spontaneous emission to state 1. If light of energy $h\nu_{32} = E_3 - E_2$ is incident on the system, absorption and stimulated emission can occur between the excited states 3 and 2. We will show that under certain conditions, a population inversion can be achieved between the two excited states (that is, $N_3 > N_2$). Such a system provides a medium for the amplification of light of energy $h\nu_{32} = E_3 - E_2$ and is said to be able to lase. The double-headed arrows indicate that both absorption and stimulated emission occur between the two states. A single B coefficient is used for absorption and stimulated emission between a set of two states because we know that $B_{ij} = B_{ji}$. Initially, all atoms are in the ground state, so that $N_1(0) = N_{total}$. We consider the case in which this three-level system is exposed to an incident light beam of spectral radiant energy density, $\rho_\nu(\nu_{31})$ (where $h\nu_{31} = E_3 - E_1$), which excites atoms from level 1 to level 3. A light beam such as this one that is used to create excited-state populations is referred to as a pump source. The pump source is assumed to have no spectral radiant energy density at $h\nu_{12} = E_2 - E_1$, and as a result no atoms are excited to state 2. Once an atom populates state 3, it can decay by stimulated emission back to state 1 (induced by the pump source) or by spontaneous emission to either state 2 or state 1. The rates of spontaneous emission to state 2 and state 1 can be different. Thus, we must include subscripts on the A coefficients to indicate explicitly the two states involved in the transition. An atom that relaxes from state 3 to state 2 can in turn relax back to the ground state by spontaneous emission.

If light of frequency ν_{32} ($h\nu_{32} = E_3 - E_2$) is available, both absorption and stimulated emission can occur between states 3 and 2. The pump source is assumed to have no spectral radiant energy density at $h\nu_{12} = E_2 - E_1$, and as a result no atoms are excited to state 2. Light of this energy is inevitably available because it is generated by the spontaneous emission process between these two levels. For a three-level system, the sum of the populations of the individual energy levels is equal to the total number of atoms:

$$N_{total} = N_1(t) + N_2(t) + N_3(t)$$

Let us consider these rate equations one by one. First consider dN_1/dt. There are four parts to the rate equation: excitation 1 → 3, stimulated emission 3 → 1, spontaneous emission 3 → 1, and spontaneous emission 2 → 1.

$$\frac{dN_1}{dt} = -B_{31}\rho_\nu(\nu_{31})N_1 + B_{31}\rho_\nu(\nu_{31})N_3 + A_{31}N_3 + A_{21}N_2 \qquad (R1)$$

Similarly, for dN_2/dt, we must take into account: spontaneous emission 3 → 2, spontaneous emission 2 → 1, stimulated emission 3 → 2, and absorption 2 → 3.

$$\frac{dN_2}{dt} = A_{32}N_3 - A_{21}N_2 + B_{32}\rho_\nu(\nu_{32})N_3 - B_{32}\rho_\nu(\nu_{32})N_2 \qquad (R2)$$

Finally, for dN_3/dt, we consider: absorption 1 → 3, stimulated emission 3 → 1, spontaneous emission 3 → 2, spontaneous emission 3 → 1, stimulated emission 3 → 2, and absorption 2 → 3.

$$\frac{dN_3}{dt} = B_{31}\rho_\nu(\nu_{31})N_1 - B_{31}\rho_\nu(\nu_{31})N_3 - A_{32}N_3 - A_{31}N_3$$
$$-B_{32}\rho_\nu(\nu_{32})N_3 + B_{32}\rho_\nu(\nu_{32})N_2 \qquad (R3)$$

Because each level is non-degenerate, the rate equations $(R1)$, $(R2)$ and $(R3)$ apply to the populations of states $1,\ 2$, and 3. When the system achieves equilibrium, the population of each level will remain constant, so that,

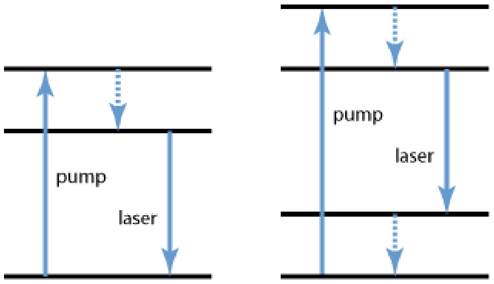
$$\frac{dN_1}{dt} = 0, \frac{dN_2}{dt} = 0, \text{ and, } \frac{dN_3}{dt} = 0$$

Although the three rate equations can be written and solved exactly to generate expressions for the time-dependent and equilibrium values of N_1, N_2 and N_3, we can learn an important result by considering only the rate equation for state 2. The population of state 2, N_2, is a balance between spontaneous emission 3 → 2 $(A_{32}N_3)$, spontaneous emission 2 → 1 $(A_{21}N_1)$, stimulated emission 3 → 2 $[B_{32}\rho_\nu(\nu_{32})N_3]$ and absorption 2 → 3 $[B_{32}\rho_\nu(\nu_{32})N_2]$. At equilibrium, $dN_2/dt = 0$, and

$$\frac{dN_2}{dt} = 0 = A_{32}N_3 - A_{21}N_2 + B_{32}\rho_\nu(\nu_{32})N_3 - B_{32}\rho_\nu(\nu_{32})N_2$$
$$\therefore N_3[A_{32} + B_{32}\rho_\nu(\nu_{32})] = N_2[A_{21} + B_{32}\rho_\nu(\nu_{32})]$$
$$\therefore \frac{N_3}{N_2} = \frac{A_{21} + B_{32}\rho_\nu(\nu_{32})}{A_{32} + B_{32}\rho_\nu(\nu_{32})}$$

Note that, N_3 can be larger than N_2 if $A_{21} > A_{32}$.

∴ A population inversion is possible between states 3 and 2 when the atoms excited to state 3 decay relatively slowly to state 2 and those in state 2 decay rapidly back to the ground state.



If this is the case, a population of state 3 can be built up, and a system of atoms that satisfies this condition may lase. Such a system is called a gain medium.