Maxwell Equations for **electrostatics**:

(ρ = charge density)

$$\boxed{\begin{aligned}\vec{\nabla}\cdot\vec{\xi} &= \frac{\rho}{\varepsilon_0}\\ \vec{\nabla}\times\vec{\xi} &= 0\end{aligned}}$$

Equivalent to **Coulomb's Law**

$$\vec{\xi} = -\vec{\nabla}\Phi = \text{- gradient of potential}$$

$$\nabla^2\Phi = -\frac{\rho}{\varepsilon_0} = \text{Gauss's Law (another form of Coulomb's Law)}$$

$$\Phi\nabla^2\Phi = -\Phi i\nabla i\nabla\Phi = -i\Phi\nabla^{\mp} i\nabla\Phi = (\nabla\ \Phi)(\nabla\Phi) = \xi^2$$

$$= \frac{\Phi\rho}{\varepsilon_0} = \text{volts} \times \text{charge density}$$

$$= \text{joule/coulomb x coulombs/volume} = \text{joules/volume}$$

$$= \textbf{energy density}$$

RELATING $\mathcal{E}_0^2$ to <u>intensity</u> of light

Energy density $\equiv u_E = \frac{\epsilon_0 \mathcal{E}_0^2}{2} = \frac{\text{Joules}}{m^3}$

Intensity $= I = u_E c$ where c = speed of light.

<u>Relate this to Fermi Golden Rule.</u>

$$\frac{P_{i\to f}}{t} = \frac{2\pi |W_{fi}|^2}{\hbar^2} \rho(\omega)$$

density of final states of molecule.

$$rate(i->f) = \frac{2\pi |\mu_{fi}|^2 |\xi_0|^2 \rho(E)}{\hbar}$$

we have seen that $|\xi_0|^2 = \frac{2}{\varepsilon_0} u(E)$

where u(E) = is the energy density in Jm^{-3}

$$rate = \frac{2\pi |\mu_{fi}|^2 \, 2u(E)\rho(E)}{\hbar\varepsilon_0}$$

$I = u(E)c$ in $\mathrm{Js}^{-1}m^{-2}$

$$rate(i->f) = \frac{2\pi |\mu_{fi}|^2 \, 2u(E)\rho(E)}{\hbar\varepsilon_0} = \frac{4\pi |\mu_{fi}|^2 \, I\rho(E)}{\hbar\varepsilon_0 \; c}$$

Consider a typical case: x_{fi} =1.0 Å =10^{-10} m
So, $|\mu_{fi}|^2 = (1.6 \times 10^{-19})^2\, 10^{-20} = 2.56 \times 10^{-58}\ C^2m^2$

Sunlight Intensity density (i.e., per nm):
$I(nm^{-1})$ = **1.0** $Js^{-1}m^{-2}$ /nm at 600 nm gives
I =1.0 Js^{-1} m^{-2} for a 1 nm band width
hbar =1.05 x 10^{-34} Js
$\varepsilon_0 = 1/ (4\pi\ 9x10^9)$
photon energy = $h\nu = hc/\lambda$ =6.62 x 10^{-34} x 3 x 10^8 /600 x 10^{-9} = 3.3 x 10^{-19} J

This leaves only $\rho(E)$ the density of states in states per J yet to find.

For a typical red fluorescent protein (Plum) we may approximate the absorption envelope as a triangle with maximum at 600 nm and base extending from 662 nm to 500 nm. This corresponds to a triangle extending from 4 x 10^{-19} to 3 x 10^{-19} J. The integral of the Franck-Condon factors =1 = ½ base x altitude = ½ x 10^{-19} J x altitude = 1.
The altitude is then = $\rho_{max}(E)$ = 2 x 10^{-19} states/J. Assume this is at 600 nm

Golden Rule therefore gives:

$$rate(i->f) = \frac{4\pi\,|\,\mu_{fi}\,|^2\ I\rho(E)}{\hbar\varepsilon_0\ \ c}$$

$$rate = \frac{4\pi(2.56\times10^{-58}C^2m^2)(1.0Js^{-1}m^{-2})(2x10^{19}states\ J^{-1})}{(1.05\times10^{-34}Js)(\frac{1}{4\pi9\times10^9}C^2J^{-1}m^{-1})\ \ 3\times10^8ms^{-1}}$$

$$= 0.23\,\text{transitions per second per molecule}$$

Check this number with Beer-Lambert Law:

dI = -2.3εC Idx which gives the familiar

$$\boxed{\frac{I}{I_0} = e^{-2.3\varepsilon Cx} = 10^{-\varepsilon Cx} = 10^{-A}}$$

A = absorbance

$$\boxed{\begin{aligned} &\frac{dIArea}{h\nu} = \frac{-2.3\varepsilon CdxArea}{h\nu}\frac{I}{h\nu} \\ &= rate(photons\,lost/\sec) = 2.3(10^5\,Lmol^{-1}cm^{-1}) \times \\ &(10^{-5}\,molL^{-1})(0.01cm)\,(1cm^2)\frac{(1.0\times10^{-4}\,Js^{-1}cm^{-2})}{3.3\times10^{-19}\,J} \\ &= 7\times10^{12}\ \text{excitations per second in volume} \end{aligned}}$$

Need to divide by total molecules in the volume

$$\text{total molecules in the volume}$$
$$= CdxArea \times \text{Avogadro's number}$$
$$= (10^{-5} molL^{-1})(10^{-3} L/cm^3)(6.02 \times 10^{23} molecules/mol)(0.01cm)(1cm^2)$$
$$= 6 \times 10^{13} \text{ molecules in volume}$$

Beer - Lambert Law therefore gives :

$$\frac{7 \text{ x } 10^{12}}{6 \text{ x } 10^{13}} = \textbf{0.12 excitations/molecule per second}$$

Fermi Golden Rule gave **0.23 excitations/molecule per second,**

within a factor of 2

Oscillating Perturbation

$$\hat{W}(t') = W_0 \cos(\omega t')$$

$$b^{(1)}(t) = \frac{-i}{\hbar} \int_0^t \hat{W}_{fi}(t') e^{i\omega_{fi} t'} dt' \qquad \text{B-20}$$

$$\cos(\omega t') = \frac{e^{i\omega t'} + e^{-i\omega t'}}{2}$$

$$b^{(1)}(t) = \frac{-iW_0}{\hbar} \int_0^t \left(\frac{e^{i(\omega_{fi} + \omega)t'} + e^{i(\omega_{fi} - \omega)t'}}{2} \right) dt'$$

$$b^{(1)}(t) = \frac{-iW_0}{\hbar} \int_0^t \left(\frac{e^{i(\omega_{fi}+\omega)t'} + e^{i(\omega_{fi}-\omega)t'}}{2} \right) dt'$$

The integral is non-zero (effectively) only when $\omega_{fi} - \omega \cong 0$ in 2nd term (ω_{fi} & ω both +) or if $\omega_{fi} + \omega \cong 0$ in 1st term (if ω_{fi} & ω are opposite sign)

In either case, the integral becomes

$$b^{(1)}(t) = \frac{-iW_0}{\hbar} \int e^{\pm i\Delta\omega t'} dt' = \frac{-iW_0}{\pm i\Delta\omega\hbar} \left(e^{\pm i\Delta\omega t} - 1 \right)$$

$$\left|b^{(1)}(t)\right|^2 = \frac{W_0^2}{(\hbar\Delta\omega)^2} 4\sin^2\left(\frac{\Delta\omega}{2}t\right)$$

i.e. as with constant W_{fi} with $\omega_{fi} \to \Delta\omega = \omega_{fi} - \omega$

i.e., Now need $\omega_{fi} = \omega$ instead of $\omega_{fi} = 0$

Excited State Radiative Lifetime (Einstein A coefficient

Consider any two states of a molecule within a container in equilibrium with electromagnetic radiation (inside a black box).

States 1 and 2 are populated with numbers of molecules N_1 and N_2 according to Boltzmann:

$$\boxed{\frac{N_2}{N_1} = e^{-\frac{(E_2 - E_1)}{kT}} = e^{-\frac{h\nu}{kT}}}$$

State 2, N_2 molecules

$\Delta E = h\nu$	Absorption rate $= N_1 B_{12} \rho(\nu)$	Spontaneous Emission rate $= N_2 A$	<u>Stimulated</u> Emission !! rate $= N_2 B_{21} \rho(\nu)$

State 1, N_1 molecules.

At <u>equilibrium</u>: $N_1 B_{12} \rho(\nu) = N_2 B_{21} \rho(\nu) + N_2 A$

The energy density $\equiv \rho(\nu) = \dfrac{8\pi h \bar{\nu}^3}{e^{\frac{h\nu}{kT}} - 1}$ ← $\bar{\nu} = \nu/c$

Planck's Blackbody Law

Einstein's brilliance here was postulating <u>stimulated</u> emission (not confirmed until the 1960's)

The last equation shows that:

$$B_{12} = B_{21} \equiv B'$$

$$A = 8\pi h \nu^3 B'$$

but B = was defined by: <u>rate</u> $= B\rho(\omega) = B'\rho(\nu)$

$$B = \frac{4\pi |M_{fi}|^2}{\hbar^2 \epsilon_0}$$

$$\rho(\omega) = \frac{d\rho}{d\omega} \qquad \rho(\nu) = \frac{d\rho}{d\nu}$$

So $\rho(\omega) = \dfrac{d\rho}{2\pi\, d\nu} = \dfrac{1}{2\pi}\rho(\nu)$

$$B\rho(\omega) = \frac{B}{2\pi}\rho(\nu) = B'\rho(\nu) \; ; \; B' = \frac{B}{2\pi}$$

$$B' = \frac{2\,|\mu_{fi}|^2}{\hbar^2 \epsilon_0}$$

$$A = \frac{8\pi h \bar{\nu}^3}{} \cdot \frac{2|\mu_{fi}|^2}{\left(\frac{h}{2\pi}\right)^2 \epsilon_0} = \frac{64\pi^3 \bar{\nu}^3 |\mu_{fi}|^2}{h\,\epsilon_0}$$

The rate of spontaneous emission depends on the <u>transition dipole squared</u> $\times$ <u>(frequency)^3</u>

Lifetime

$$\text{rate} = \frac{dN}{dt} = -AN$$

$$\frac{N(t)}{N(0)} = e^{-At} = e^{-\frac{t}{\tau}}$$

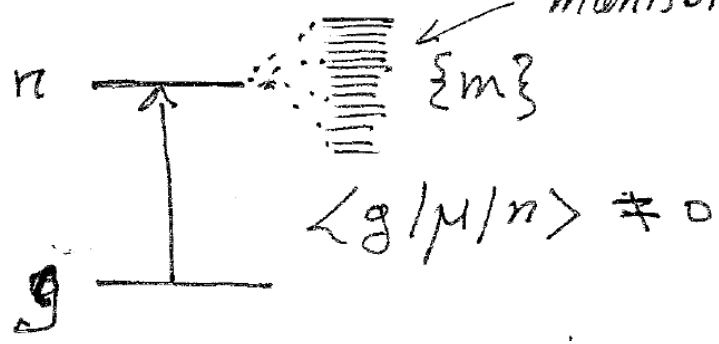
where τ = "lifetime" = $\frac{1}{A}$

Your next homework problem, Due next Wed. will contain this problem and other

Exercise: (a) Find the radiative lifetime for an excited state for which the transition dipole length = 1 Å at a wavelength of 500 nm.

(b) Compare your result to a transition at $\bar{\nu} = 1\ cm^{-1}$ with the same μ_{fi}.

(B) The LIFETIME OF a COHERENTLY EXCITED SUPERPOSITION.



$$\langle g|\mu|m\rangle = 0$$

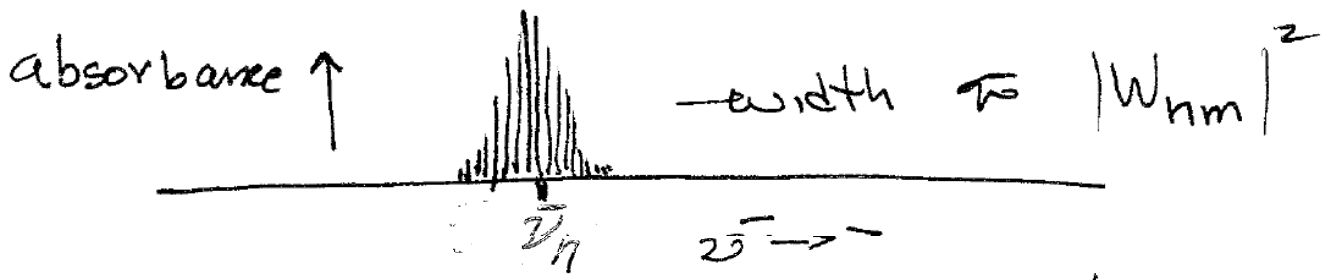
$$\mathcal{H} = H_0 + W$$

$$H_0|n\rangle = E_n|n\rangle \qquad H_0|m\rangle = E_m|m\rangle$$

$$\langle n|W|m\rangle \neq 0 = W_{nm}$$

Molecular Eigen states $= \psi_i = b_{n_i}|n\rangle + \sum_m b_{m_i}|m\rangle$

So a <u>band</u> of eigenstates is observed whose spectrum will look like:



rate of absorption to state ψ_i is $\propto |\langle g|\mu|\psi_i\rangle|^2$

$$\propto \left|\langle g|\mu|\left(b_{ni}|n\rangle + \sum_m b_{mi}|m\rangle\right)\right|^2$$

$$\propto b_{ni}^2 |\langle g|\mu|n\rangle|^2$$

rate of absorption to state ψ_i is $\propto |\langle g|\mu|\psi_i\rangle|^2$

$$\propto \left|\langle g|\mu|\left(b_{ni}|n\rangle + \sum_m b_{mi}|m\rangle\right)\right|^2$$

$$\propto b_{ni}^2 |\langle g|\mu|n\rangle|^2$$

For equally spaced levels of $\{m\}$ and a constant interaction W_{nm}

$$b_{ni}^2 \propto \frac{\Delta^2}{\Delta^2 + (\bar{\nu}_i - \bar{\nu}_n)^2} \quad \text{(a Lorenzian)}$$

Note half width at half maximum = Δ

Now if a pulse of radiation is applied such that the spectral width is $\Delta\bar{\nu} \gg 2\Delta$, centered at $\bar{\nu}_n$

all the ψ_i are coherently excited, producing the wavepacket

$$\boxed{\Psi_{(t)} \propto \sum_i \langle g|\mu|n\rangle\, b_{ni}\, \psi_i\, e^{-i\omega_i t}}$$

$$\propto |\langle g|\mu|n\rangle| \sum_i b_{ni}^2\, e^{-i\omega_i t}$$

$\propto |\mu_{gn}|^2$ at time $t=0$ since $\sum_i b_{ni}^2 = 1$

$$\propto |\langle g|\mu|n\rangle| \sum_i^2 b_{ni}^2 \, e^{-i\omega_i t}$$

$\propto |\mu_{gn}|^2$ at time $t=0$ since $\sum_i b_{ni}^2 = 1$

<u>Dephasing</u> occurs as time increases and the different ψ_i parts get out of phase.

Note that because of close spacing.

$$\sum_i b_{ni}^2 e^{-i\omega_i t} \Rightarrow \int b_n^2(\omega_i)\, e^{-i\omega_i t}\, d\omega_i$$

= Fourier transform of a Lorenzian

$$\int_{-\infty}^{\infty} \frac{\cos \omega t}{1+\omega^2} = \pi e^{-t} = \text{exponential}$$

$$\int \frac{\Delta^2 \cos \omega t\, d\omega}{\Delta^2 + \omega^2} = \Delta \int \frac{\cos \frac{\omega}{\Delta} \Delta t \; d\frac{\omega}{\Delta}}{1 + \left(\frac{\omega_0 - \omega}{\Delta}\right)^2} = \Delta e^{-\Delta t}$$

So emission decays exponentially

rate $\propto e^{-\Delta t} = e^{-t/\tau}$ $\qquad \tau = \frac{1}{\Delta}$

$$\Delta \propto \left|\frac{W_{nm}}{\hbar}\right|^2$$

W_{nm} can be interaction with radiation field. in which this describes spontaneous and stimulated emission.

or m may be high vibrational levels of a lower electronic state. Then

τ^{-1} = a non-radiative rate.