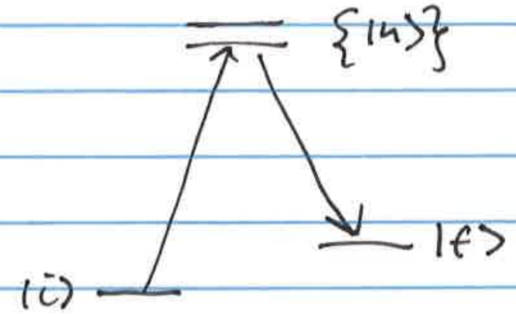
Optics & Spectroscopy — Lecture 17

Consider the following scheme:



several different ways we can go from $|i\rangle$ to $|f\rangle$

eg 2 levels: $|1\rangle$, $|2\rangle$

we can do: $|i\rangle \to |1\rangle \to |f\rangle$

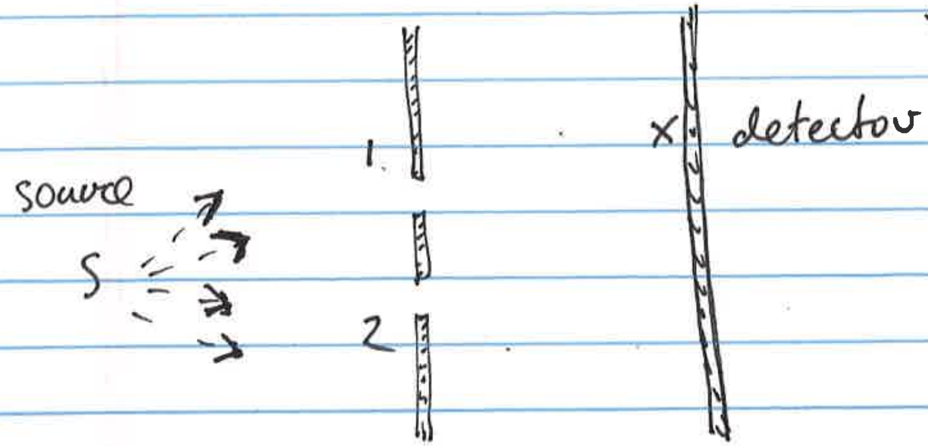
or $|i\rangle \to |2\rangle \to |f\rangle$

Prob^y for the 1st process: $\sim \underbrace{\langle f|\mu|1\rangle}_{|f\rangle \leftarrow |1\rangle}\underbrace{\langle 1|\mu|i\rangle}_{|1\rangle \leftarrow |i\rangle}$

Prob^y for the 2nd process: $\sim \underbrace{\langle f|\mu|2\rangle}_{|f\rangle \leftarrow |2\rangle}\langle 2|\mu|i\rangle$

$|2\rangle \leftarrow |i\rangle$

Now consider the 2-slit experiment w/ electrons



Feynman "Lectures on Physics" Vol. III

Prob^y elec. leaves S and arrives at x $= \langle x|s\rangle$

~ 2 pathways, we have to add these at the amplitude level

$$\langle x|s\rangle = \underbrace{\langle x|1\rangle\langle 1|s\rangle}_{\text{through } 1} + \underbrace{\langle x|2\rangle\langle 2|s\rangle}_{\text{through } 2}$$

write: $\phi_1 = \langle x|1\rangle\langle 1|s\rangle$

$\phi_2 = \langle x|2\rangle\langle 2|s\rangle$

Prob: $|\langle x|s\rangle|^2 = |\phi_1 + \phi_2|^2$

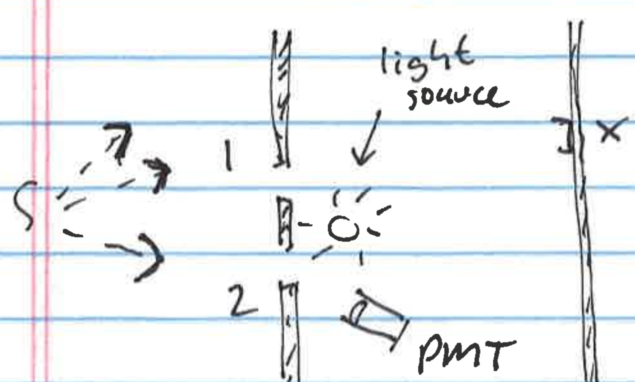
$$= \phi_1^2 + \phi_2^2 + \underbrace{\phi_1^* \phi_2 + \phi_1 \phi_2^*}_{\text{"interference" terms.}}$$

Note: $\langle \vec{r}_2 | \vec{r}_1 \rangle \sim \dfrac{e^{i\vec{k}\cdot\vec{r}_{12}}}{\vec{r}_{12}}$

$\Rightarrow \phi_1^* \phi_2 + \phi_1 \phi_2^*$ ~ oscillate as a f= of distance

~ see an interference pattern when these terms are present

~ imagine we now do an experiment where we try to determine which "slit" the electron goes through



← set up a detector so we can detect scattered photons when e^- goes through 2

~ prob^{y} amplitude we detect a photon when electron goes through "1" $= a$

~ prob^{y} amplitude we detect a photon when electron goes through "2" $= b$

~ perfect experiment $a = 0$; $b = 1$

Now prob^{y} amplitude electron goes from s to x and we detect a photon

$$\langle x|1\rangle a \langle 1|s\rangle + \langle x|2\rangle b \langle 2|s\rangle = a\phi_1 + b\phi_2$$

$$\text{Prob}^{y} = |a\phi_1 + b\phi_2|^2 = a^2\phi_1^2 + b^2\phi_2^2 + ab(\phi_1^*\phi_2 + \phi_1\phi_2)$$

~ for a well designed experiment ($a=0$)

$$\text{Prob}^{y} = b^2\phi_2^2$$ ~ no interference

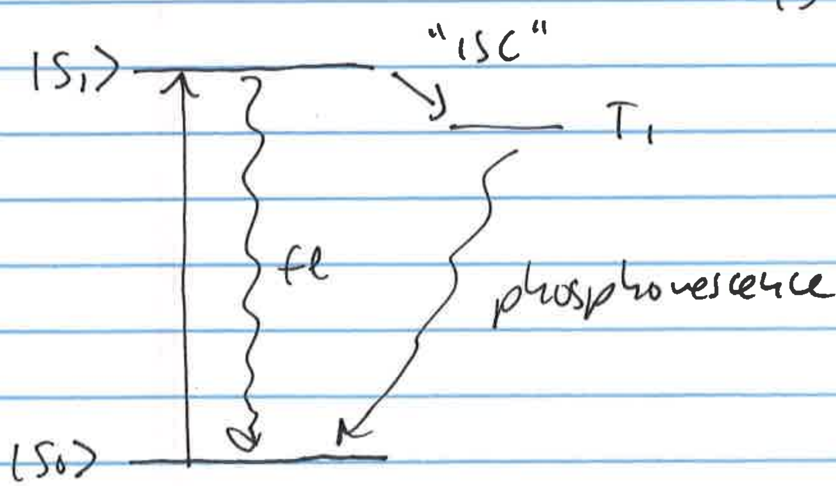
~ if we measure the pathway, we lose the interference effect

~ only see interference when we don't know whether the electron went through slit 1 or slit 2

Back to our molecular example

"Jablonski Diagram"

"ISC" ~ Intersystem crossing



ISC ~ occurs b/c of mixing b/w the singlet & triplet states lifetime of S_1: $[S_1] = [S_1]_0 \, e^{-(k_{isc} + k_{fl})t}$

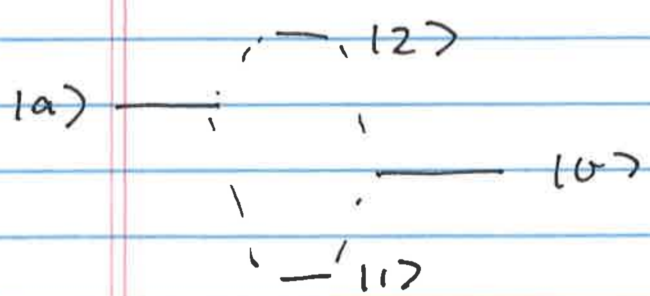
$$\tau = \frac{1}{k_{isc} + k_{fl}}$$

Quantum Yield: $Q = k_{fl} / k_{fl} + k_{isc} < 1$

~ measure τ & Q we can determine k_{fl} & k_{isc}

~ Note: $k_{isc} \uparrow$ $\tau \downarrow$ & $Q \downarrow$

~ mixing means the molecular eigenstates are not "pure" singlets or triplets



lets say $|a\rangle$ is a "bright state"

$|a\rangle = |S_1\rangle$

$|b\rangle$ is a "dark state"

$|b\rangle = |T_1\rangle$

by "bright" and "dark" we mean

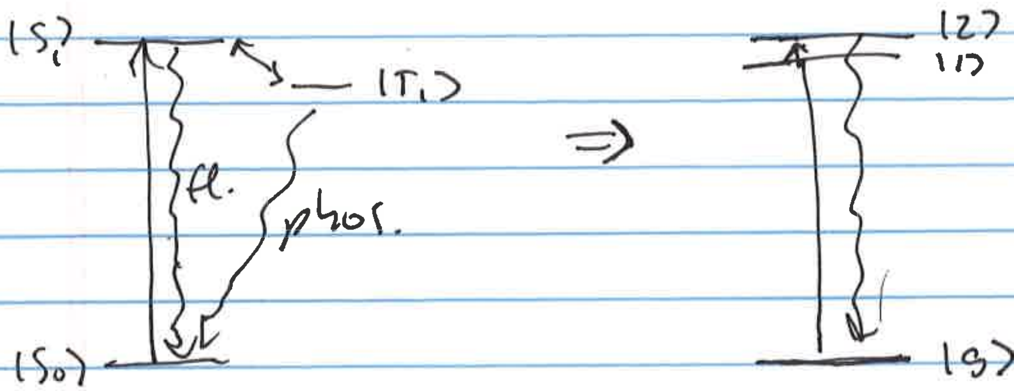
$$\langle a | \vec{\mu} | g \rangle \neq 0$$

$$\langle b | \vec{\mu} | g \rangle = 0$$

$|1\rangle$ + $|2\rangle$ are the true eigenstates

~ eigenstates of the complete Hamiltonian

$$\hat{H} = \hat{H}_0 + \hat{V}_{SO}$$ spin-orbit coupling



~ we can write $|1\rangle$ + $|2\rangle$ in terms of $|a\rangle$ and $|b\rangle$

$$|1\rangle = -\alpha|a\rangle + \beta|b\rangle$$

$$|2\rangle = \beta|a\rangle + \alpha|b\rangle$$

Likewise:

$$|a\rangle = -\alpha|1\rangle + \beta|2\rangle$$

$$|b\rangle = \beta|1\rangle + \alpha|2\rangle$$

~ excite the system we create a wavefunction

$$|\psi(t)\rangle = \sum_n C_n(t)\, e^{-iE_n t/\hbar} |n\rangle$$

$|n\rangle$ ~ $|1\rangle$ and $|2\rangle$, not $|a\rangle, |b\rangle$

~ eigenstates of the true Hamiltonian

as before: $C_n(t) = -\frac{i}{\hbar} \int_{-\infty}^{t} dt' e^{i\omega_{ng} t'} \langle n | V(t) | g \rangle$

$V(t) = \frac{\mathcal{E}(t)}{2} \left(e^{-i\omega t} + e^{i\omega t} \right) \hat{\epsilon} . \vec{\mu}_{ng}$

now allow the light source to have a time dependence

2 cases: (i) $\mathcal{E}(t) = \mathcal{E}_0$ ~ continuous

~ narrow ν

(ii) $\mathcal{E}(t) = \delta(t)$ ~ delta function

~ ultrafast pulse

$C_n(t) = \frac{-i}{\hbar} \frac{\hat{\epsilon} . \vec{\mu}_{ng}}{2} \int_{-\infty}^{t} dt' \, \mathcal{E}(t') \left\{ e^{i(\omega_{ng} - \omega)t'} + e^{i(\omega_{ng} + \omega)t'} \right\}$

c) $\mathcal{E}(t) = E_0$

$$|C_n|^2 = \frac{|\hat{\epsilon}\cdot\vec{\mu}_{ng}|^2}{\hbar^2} \frac{\sin^2 \Delta t/2}{\Delta^2}$$

~ prob of making a transition to $|1\rangle$ or $|2\rangle$ depends on resonance (Δ) and $\vec{\mu}_{ng} = \langle n|\vec{\mu}|g\rangle$

$$\langle 1|\vec{\mu}|g\rangle = \{-\alpha\langle a| + \beta\langle b|\}\vec{\mu}|g\rangle$$

$$= -\alpha\langle a|\vec{\mu}|g\rangle \qquad (\langle b|\vec{\mu}|g\rangle = 0)$$

$$\langle 2|\vec{\mu}|g\rangle = \{\beta\langle a| + \alpha\langle b|\}\vec{\mu}|g\rangle$$

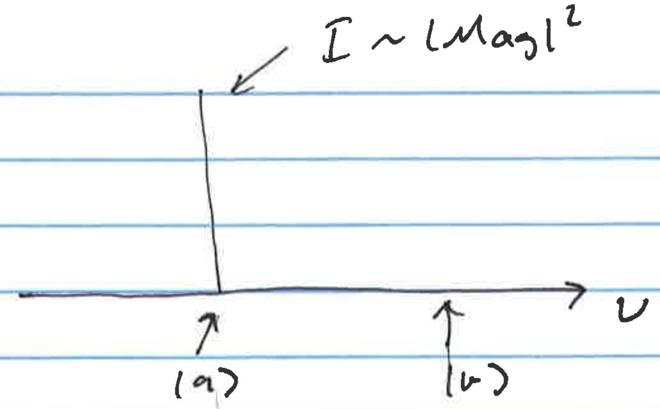
$$= \beta\langle a|\vec{\mu}|g\rangle$$

$$|C_1|^2 \sim |\mu_{1g}|^2 = \alpha^2|\mu_{ag}|^2$$

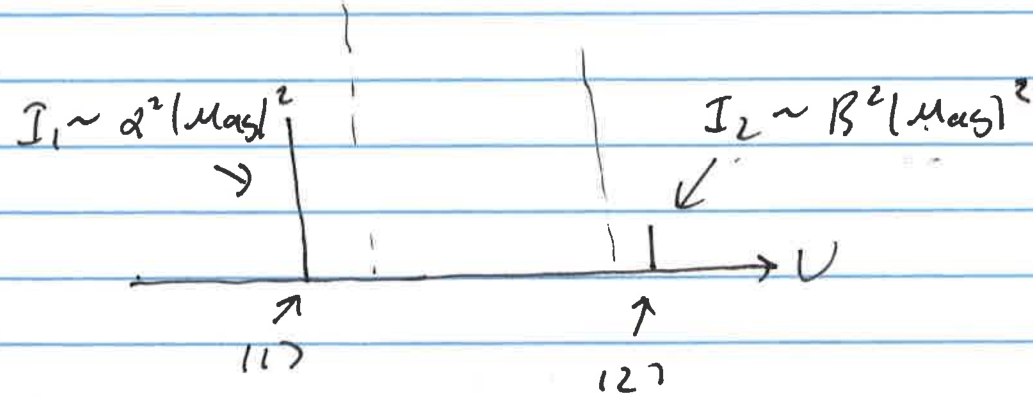
$$|C_2|^2 \sim |\mu_{2g}|^2 = \beta^2|\mu_{ag}|^2$$

~ consider how spectra look with and without coupling

No coupling:



With coupling:



Total Intensity: $I_1 + I_2 = \alpha^2 |M_{ag}|^2 + \beta^2 |M_{ag}|^2$

$$= (\alpha^2 + \beta^2) |M_{ag}|^2$$

$$= |M_{ag}|^2$$

~ intensity is not lost when we have couplings ~ just moved around

c(ii) δ function excitation

δ - function ~ spectrally broad

~ excite all the transitions

$$C_n(t) = \frac{-i\,\hat{\epsilon}\cdot\vec{\mu}_{ng}}{2\hbar} \int_{-\infty}^{t'} dt'\, \delta(t') \times \left\{ e^{i(\omega_{ng}-\omega)t'} + e^{i(\omega_{ng}+\omega)t'} \right\}$$

~ just after the laser pulse $(C_n(t=0))$

$$C_n(0) = \frac{-i}{\hbar}\, \hat{\epsilon}\cdot\vec{\mu}_{ng}$$

$$|\psi(t=0)\rangle = C_1(0)|1\rangle + C_2(0)|2\rangle$$

$$= \frac{-i\hat{\epsilon}\cdot}{\hbar}\left[\langle 1|\vec{\mu}|g\rangle|1\rangle + \langle 2|\vec{\mu}|g\rangle|2\rangle\right]$$

$$= \frac{-i\,\hat{\epsilon}\cdot\vec{\mu}_{ag}}{\hbar}\left[-\alpha|1\rangle + \beta|2\rangle\right]$$

δ-function creates a coherent superposition of $|1\rangle$ and $|2\rangle$

Note! $|1\rangle = -\alpha|a\rangle + \beta|b\rangle$

$|2\rangle = \beta|a\rangle + \alpha|b\rangle$

$$|\psi(0)\rangle = \frac{-i\,\hat{\epsilon}\cdot\vec{\mu}_{ag}}{\hbar}\left\{ -\alpha\left(-\alpha|a\rangle + \beta|b\rangle\right) + \beta\left(\beta|a\rangle + \alpha|b\rangle\right)\right\}$$

$$= (\quad)\left\{ \alpha^2|a\rangle - \alpha\beta|b\rangle + \beta^2|a\rangle + \alpha\beta|b\rangle \right\}$$

$$= (\ )\left\{ (\alpha^2+\beta^2)|a\rangle \right\}$$

$$= \frac{-i\,\hat{\epsilon}\cdot\vec{\mu}_{ag}}{\hbar}|a\rangle$$ ← system is initially created in the "zeroth-order" bright state

~ but this state is not an eigenstate of the complete Hamiltonian
⇒ it evolves in time

$|\psi(0)\rangle = |a\rangle$ (drop $\frac{-i\hat{\epsilon}\cdot\vec{\mu}_{ag}}{\hbar}$)

$= -\alpha|1\rangle + \beta|2\rangle$

$$|\psi(t)\rangle = -\alpha|1\rangle e^{-iE_1t/\hbar} + \beta|2\rangle e^{-iE_2t/\hbar}$$

Prob^y of finding the system in $|1\rangle$ or $|2\rangle$

$$\left.\begin{array}{l} |C_1|^2 = |\langle 1|\psi(t)\rangle|^2 = \alpha^2 \\ |C_2|^2 = |\langle 2|\psi(t)\rangle|^2 = \beta^2 \end{array}\right\} \text{constant w/ time}$$

Prob^y of detecting a photon?

$$\text{Prob}^y \sim |\langle g|\vec{\mu}|\psi(t)\rangle|^2$$

$$\left.\begin{array}{l} \langle g|\vec{\mu}|1\rangle = -\alpha\langle g|\vec{\mu}|a\rangle \\ \langle g|\vec{\mu}|2\rangle = \beta\langle g|\vec{\mu}|a\rangle \end{array}\right\} \leftarrow$$

this "picks out" the $|a\rangle$ part of $|\psi\rangle$

$$|\langle g|\vec{\mu}|\psi(t)\rangle|^2 = \Big|-\alpha\langle g|\vec{\mu}|1\rangle e^{-iE_1t/\hbar} + \beta\langle g|\vec{\mu}|2\rangle e^{-iE_2t/\hbar}\Big|^2$$

$$= |\vec{\mu}_{ga}|^2\Big|\alpha^2 e^{-iE_1t/\hbar} + \beta^2 e^{-iE_2t/\hbar}\Big|^2$$

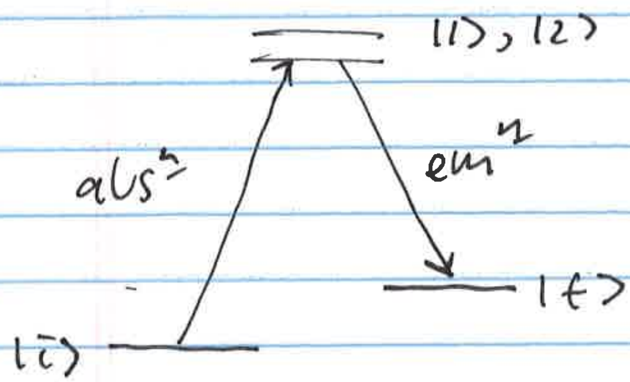
$$= |\vec{\mu}_{ga}|^2\left(\alpha^2 e^{-iE_1t/\hbar} + \beta^2 e^{-iE_2t/\hbar}\right) \times \left(\alpha^2 e^{iE_1t/\hbar} + \beta^2 e^{iE_2t/\hbar}\right)$$

$$\text{Prob}^4 \sim \alpha^4 + \beta^4 + \alpha^2\beta^2\left(e^{-i(E_1-E_2)t/\hbar} + e^{i(E_1-E_2)t/\hbar}\right)$$

$$= \alpha^4 + \beta^4 + 2\alpha^2\beta^2 \cos\omega_{12} t$$

not constant in time!

~ oscillation in time represent interference b/w the 2 pathways to go from the initial state to the final state



Pathways:

$|i\rangle \to |1\rangle \to |f\rangle$

or $|i\rangle \to |2\rangle \to |f\rangle$

~ if we use a monochromatic light source ($E(t) = E_0$), we can determine which pathway we used ~ no interference

Chem. Soc. Rev. 2000, 29, 305-314

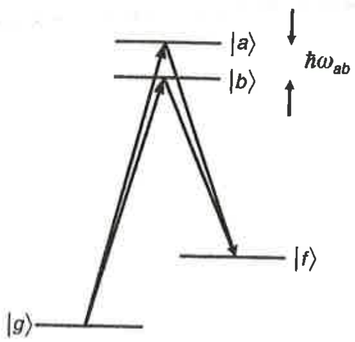


Fig. 1 Diagram of the four level system. A photon is absorbed by the ground state $|b\rangle$ and excites a superposition of states $|a\rangle$ and $|b\rangle$ whose energy separation is $\Delta E = \hbar\omega_{ab}$. Emission of a second photon leaves the system in the final state $|f\rangle$.

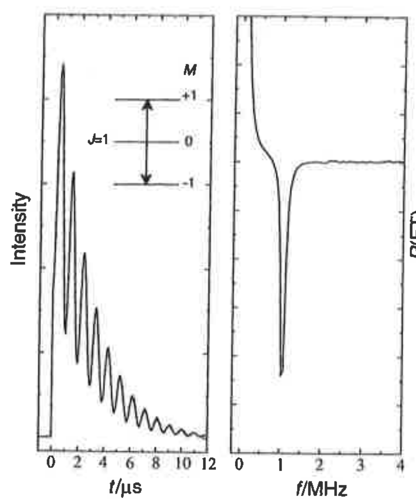


Fig. 2 Zeeman quantum beat recorded for the $R(0)$ line of the 17U transition in CS_2 in an external field of ~15 Gauss. The laser polarisation was perpendicular to the magnetic field direction and prepares a coherence between the $M = \pm1$ sublevels as shown in the level diagram. This is manifested by a single quantum beat on the fluorescence decay; the real part of the Fourier transform is also shown. The less than 100% modulation, which is observed in virtually all quantum beat measurements in molecules, is due to incoherent emission from the excited states.

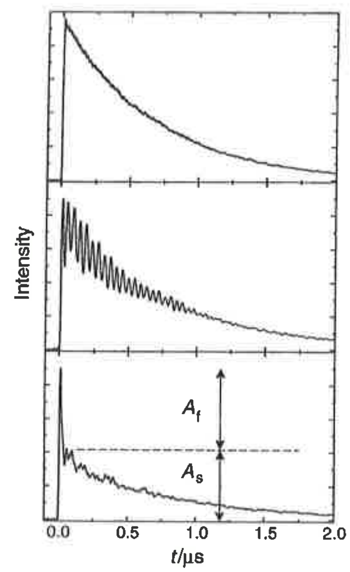


Fig. 9 Fluorescence decays recorded in the $6a_0^1 6b_0^2$ vibrational band of the $S_1 \leftarrow S_0$ transition in pyrimidine for different upper state rotational levels, from the left with $J = 0, 2$ and 5 respectively. Coupling of singlet and triplet levels results in eigenstates and the decays exhibit a transition in appearance from exponential (single eigenstate), through quantum beats (few eigenstates) to biexponential (many eigenstates). The arrows in the lower decay illustrate the concept of fast and slow components in a biexponential decay.