Emission and Absorption of Radiation

$\vec{E} = E_0 \cos(\omega t)\hat{k}$ ignore spatial part. Why

$n=1 \to n=2$ 10.2 eV $\to$ 1219 Å, diameter atom $\approx 1°$

$H' = -qE_0 z \cos(\omega t)$ $q = -|e|$

$E = -q\int E \cdot dr \to$ Work done by Electric Field

$H'_{ba} = -pE_0 \cos(\omega t)$ $p = q\langle \psi_b | z | \psi_a \rangle$

Note ψ_a and ψ_b are manifestly $\psi_{nem} = R_{ne}(r) Y_e^m(\theta,\phi)$

Typically $z|\psi|^2$ is odd so $H'_{aa} = H'_{bb} = 0$

We have seen this

$$P_{a \to b}(t) = |C_b(t)|^2 \simeq \frac{|V_{ab}|^2}{\hbar^2} \frac{\sin^2[(\omega_0 - \omega)t/2]}{(\omega_0 - \omega)^2}$$

$$V_{ab} = -pE_0 = -qE_0 \langle \psi_b | z | \psi_a \rangle$$

Ex $\to$ $\psi_{100} \to \psi_{200}$? Can $n=2 \to n=1$ happen?

$-qE_0 \langle \psi_{100} | z | \psi_{200} \rangle$?

$$\psi_{100} = \frac{1}{\sqrt{\pi a^3}} e^{-r/a} \quad \psi_{200} = \frac{1}{\sqrt{8\pi a^3}}\left(1-\frac{r}{2a}\right)e^{-r/2a} \quad z = r\cos\theta$$

$$\langle \psi_{100} | z | \psi_{200} \rangle = \frac{1}{2\pi a^3}\frac{1}{\sqrt{2}} \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \overset{z}{r\cos\theta}\left(1-\frac{r}{2a}\right)e^{-3r/2a}\, r^2 \sin\theta \, d\theta \, d\phi \, dr$$

$$\langle \psi_{100} | z | \psi_{200} \rangle \rightarrow \int_0^{\pi} r\cos\theta \sin\theta \, d\theta \quad \text{let } u = \sin\theta \quad du = \cos\theta$$

$$u = 0, 0$$

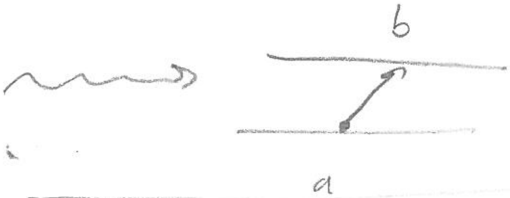
$$\int_0^0 u\,du = \frac{u^2}{2}\Big|_0^0 = 0 \quad = 0$$

$$P_{\psi_{100} \to \psi_{200}} = 0 \quad ?$$

Start in ψ_a Shine monochromatic light

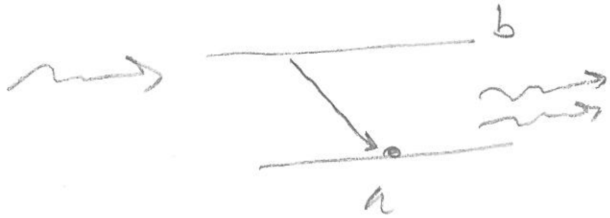
with frequency ω

$$P_{a\to b} = \left(\frac{|P|E_0}{\hbar}\right)^2 \frac{\sin^2[(\omega_0-\omega)t/2]}{(\omega_0-\omega)^2}$$



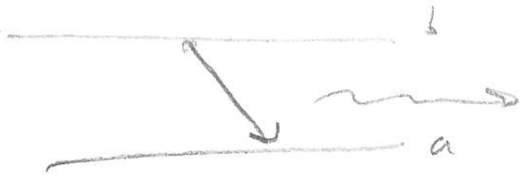
Stimulated absorption

$P_{b\to a}$? SAME. HUH



Stimulated emission

lasers



Spontaneous Emission

Incoherent Perturbations

$$\frac{\text{Energy}}{\text{Volume}} = U = \frac{\epsilon_0}{2} E_0^2$$

$$P_{b-a}(T) = \frac{2U}{\epsilon_0 \hbar^2} |p|^2 \frac{\sin^2[(\omega_0-\omega)T/2]}{(\omega_0-\omega)^2} \qquad p = q\langle \psi_b | z | \psi_a \rangle$$

Not Monochromatic? $u \to \rho(\omega)\,d\omega$ energy density in range $d\omega$

Then $$P_{b-a}(T) = \frac{2}{\epsilon_0 \hbar^2} |p|^2 \int_0^\infty \rho(\omega) \frac{\sin^2((\omega_0-\omega)T/2)}{(\omega_0-\omega)^2} d\omega$$

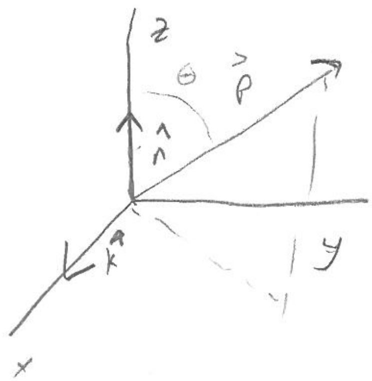
Or $$P_{b-a}(T) \sim \frac{2|p|^2}{\epsilon_0 \hbar^2} \rho(\omega_0) \int \frac{\sin^2[(\omega_0-\omega)T/2]}{(\omega_0-\omega)^2} d\omega$$

Let $x = (\omega_0-\omega)\frac{T}{2}$ and $\int \frac{\sin^2 x}{x^2} dx = \pi$

$$P_{b-a}(T) \simeq \frac{\pi |p|^2}{\epsilon_0 \hbar^2} \rho(\omega_0)\, T \to \frac{dP}{dT} = R_{b-a} = \frac{\pi |p|^2}{\epsilon_0 \hbar^2} |p^2| \rho(\omega_0)$$

What if atom is bathed by light from all directions!

Want $p = q\langle \psi_b | \vec{r} | \psi_a \rangle \to |\vec{p}\cdot\hat{n}|^2$



$\vec{p}\cdot\hat{n} = |p|\cos\theta$

$$|\vec{p}\cdot\hat{n}|^2_{avg} = \frac{1}{4\pi}\int |p|^2\cos^2\theta\sin\theta\,d\theta\,d\phi = \frac{|p|^2}{4\pi}\left(-\frac{\cos^3\theta}{3}\right)\Big|_0^{\pi} \cdot 2\pi = \frac{1}{3}|p|^2$$

$$R_{b\to a} = \frac{\pi}{3\epsilon_0\hbar^2}|p|^2\rho(\omega_0)$$

Einstein A and B coefficients

Let N_a be # in state ψ_a and N_b be # in state ψ_b

A is the spontaneous emission coefficient

What is $\frac{dN_b}{dt}$?

$$\frac{dN_b}{dt} = -N_b A - N_b B_{ba}\rho(\omega_0) + N_a B_{ab}\rho(\omega_0)$$

leaving b spontaneously

leaving b due to radiation field

entering b due to radiation field

I The System is in Thermal equilibrium

$$\frac{dN_b}{dT} = 0$$

$$-N_b A - N_b B_{ba}\,\rho(\omega_0) + N_a B_{ab}\,\rho(\omega_0) = 0$$

$$\rho(\omega_0) = \frac{N_b A}{N_a B_{ab} - N_b B_{ba}} = \frac{A}{\left(\frac{N_a}{N_b}\right) B_{ab} - B_{ba}}$$

but $\frac{N_a}{N_b} = \frac{e^{-E_a/k_bT}}{e^{-E_b/k_bT}} = e^{\hbar\omega_0/k_bT}$ → Thermal Equilibrium

So $$\rho(\omega_0) = \frac{A}{e^{\hbar\omega_0/k_bT} B_{ab} - B_{ba}}$$

From The Planck Formula $\rho(\omega) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\hbar\omega/k_bT} - 1}$

So $B_{ab} = B_{ba}$ and $\boxed{A = \frac{\omega_0^3 \hbar}{\pi^2 c^3} B_{ba}}$

$\boxed{B_{ba} = \frac{\pi}{3\epsilon_0 \hbar^2} |P|^2}$ So $\boxed{A = \frac{\omega_0^3 |P^2|}{3\pi\epsilon_0 \hbar c^3}}$

Lifetimes

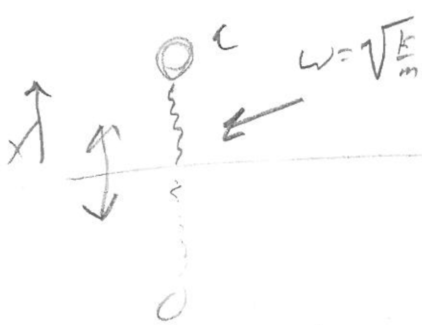
For No external radiation a System in State b will evolve as $\frac{dN_b}{dt} = -AN_b$ or $N_b(t) = N_b(0)e^{-At}$

τ = lifetime $= \frac{1}{A}$ $\quad N_b(\tau) = \frac{1}{e}N_b(0)$

For many pathways $\tau \sim \frac{1}{A_1 + A_2 + A_3 + \cdots}$

$$\vec{P} = q\langle n|x|n'\rangle\hat{i}$$

$$\vec{P} = q\sqrt{\frac{\hbar}{2m\omega}}\left(\sqrt{n'}\,\delta_{n,n'-1} + \sqrt{n}\,\delta_{n',n-1}\right)$$



emission $n \to n'$

$$\vec{P} = q\sqrt{\frac{\hbar}{2m\omega}}\sqrt{n}\,\delta_{n',n-1}$$

$$\omega_0 = \frac{E_n - E_{n'}}{\hbar} = \frac{(n+\frac{1}{2})\hbar\omega - (n'+\frac{1}{2})\hbar\omega}{\hbar} = (n-n')\omega = \underline{\omega}$$

$n' = n-1$

radiates at ω

$$A = \frac{n q^2 \omega^2}{6\pi\epsilon_0 m c^3} \qquad \tau_n = \frac{1}{A}$$

$$\text{Power} = \hbar\omega A = \frac{q^2\omega^2}{6\pi\epsilon_0 m c^3}(n\hbar\omega)$$

A, E 1 photon

$$E_n = (n+\tfrac{1}{2})\hbar\omega \quad \text{So} \quad P_q = \frac{q^2\omega^2}{6\pi\epsilon_0 m c^3}\left(E_n - \frac{1}{2}\hbar\omega\right)$$

$$P_{classical} = \frac{q^2\omega^2}{6\pi\epsilon_0 m c^3} E_n$$

For Quantum $E_n = \frac{1}{2}\hbar\omega$

So $P_q = 0$

Ground State Protected

Selection Rules $\rightarrow$ $\psi_{n\ell m_\ell} \rightarrow \psi_{n'\ell' m_\ell'}$?

$\langle \psi_b | \vec{r} | \psi_a \rangle$ or $\langle n'l'm' | \vec{r} | n\ell m \rangle$ $\rightarrow$ ugly

$\sim \langle n'\ell'm' [x + y + z] n\ell m \rangle$

<u>Trick time</u>

$[L_z, x] = i\hbar y$, $[L_z, y] = -i\hbar x$ $[L_z, z] = 0$

So $\underline{\underline{\#1.}}$ $\langle n'\ell'm' | [L_z, z] | n\ell m \rangle = 0$

but $\langle n'\ell'm' | L_z z - z L_z | n\ell m \rangle = \langle n'\ell'm' | m'\hbar z - z m\hbar | n\ell m \rangle$

$= (m' - m)\hbar \langle n'\ell'm' | z | n\ell m \rangle$

Either $m' = m$ or $\langle n'\ell'm' | z | n\ell m \rangle = 0$

So $m' = m$ is a rule or $\langle n'\ell'm' | z | n\ell m \rangle$ is 0

$\underline{\underline{\#2.}}$ $\langle n'\ell'm' | [L_z, x] | n\ell m \rangle = \langle n'\ell'm' | L_z x - x L_z | n\ell m \rangle$

$= \hbar(m' - m) \langle n'\ell'm' | x | n\ell m \rangle = i\hbar \langle n'\ell'm' | y | n\ell m \rangle$

Or $\langle n'\ell'm' | x | n\ell m \rangle (m' - m) = i \langle n'\ell'm' | y | n\ell m \rangle$

3.

$$\langle n'\ell'm'|[L_z,y]|n\ell m\rangle = \langle n'\ell'm'|L_z y - yL_z|n\ell m\rangle$$

$$= (m'-m)\hbar\,\langle n'\ell'm'|y|n\ell m\rangle = -i\hbar\,\langle n'\ell'm'|x|n\ell m\rangle$$

Now $(m'-m)\langle n'\ell'm'|y|n\ell m\rangle = -i\langle n'\ell'm'|x|n\ell m\rangle$

and

$i\langle n'\ell'm'|y|n\ell m\rangle = (m'-m)\langle n'\ell'm'|x|n\ell m\rangle$

Combining

$(m'-m)^2\langle n'\ell'm'|x|n\ell m\rangle = \langle n'\ell'm'|x|n\ell m\rangle$

True iff $\langle n'\ell'm'|x|n\ell m\rangle = \langle n'\ell'm'|y|n\ell m\rangle = 0$

or $(m'-m)^2 = 1$ or $\Delta m = \pm 1$

So $\psi_a \leftrightarrow \psi_b$ iff $\Delta m = 0, \pm 1$

Photons are spin one bosons

Conservation of spin requires

atom gives up what photon takes and vice

versa

ℓ and ℓ' ?

given $\quad [L^2,[L^2,r]] = 2\hbar^2(rL^2+L^2r)$

Same $\langle n'\ell'm'|[L^2,[L^2,r]]|n\ell m\rangle = 2\hbar^2\langle n'\ell'm'|\,rL^2+L^2r\,|n\ell m\rangle$

$$= 2\hbar^2\left[\hbar^2\ell'(\ell'+1)+\hbar^2\ell(\ell+1)\right]\langle n'\ell'm'|r|n\ell m\rangle$$

but $\langle n'\ell'm'|[L^2,[L^2,r]]|n\ell m\rangle = \langle n'\ell'm'|L^2[L^2,r]-[L^2,r]L^2|n\ell m\rangle$

$= \hbar^2(\ell'(\ell'+1)-\ell(\ell+1))\langle n'\ell'm'|[L^2,r]|n\ell m\rangle$

$= \hbar^2(\ell'(\ell'+1)-\ell(\ell+1))\langle n'\ell'm'|L^2r-rL^2|n\ell m\rangle$

$= \hbar^4(\ell'(\ell'+1)-\ell(\ell+1))^2\langle n'\ell'm'|r|n\ell m\rangle$

So either $\quad \langle n'\ell'm'|r|n\ell m\rangle = 0$

or $\quad 2\left[\ell'(\ell'+1)+\ell(\ell+1)\right] = \left[\ell'(\ell'+1)-\ell(\ell+1)\right]^2$

Satisfied for $\ell' = \ell\pm1$

$\Delta\ell = \pm1$