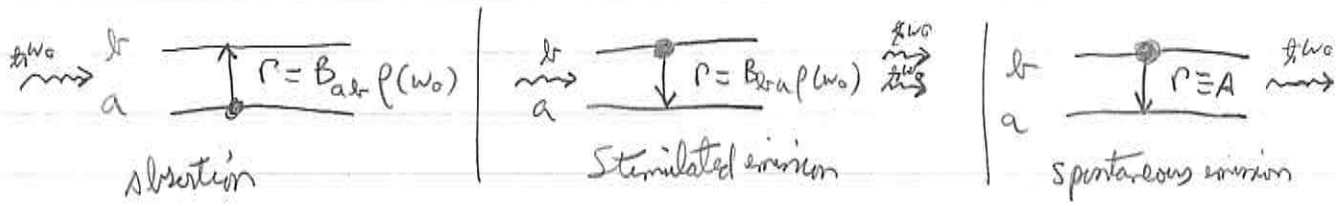
P423 – Lecture 19: Spontaneous emission, selection rules



Calculation of spontaneous emission rate using the idea of detailed balance: That the value of A must be set so that the equilibrium population of photons is described by the blackbody formula:

$$\rho(\omega_0) = \frac{\hbar}{\pi^2 c^3}\,\frac{\omega^3}{e^{\frac{\hbar\omega}{k_B T}} - 1}$$

Assume there are N_a atoms in the state a, and N_b in state b. The rate of change of N_b is given by:

Note: A has dimension of $\frac{1}{\text{time}}$!

$$\frac{dN_b}{dt} = \underbrace{-N_b A}_{\substack{\text{Spontaneous emission} \\ \text{out of level b}}} \;\underbrace{-\,N_b B_{ba}\,\rho(\omega_0)}_{\text{Stimulated}} + \underbrace{N_a B_{ab}\,\rho(\omega_0)}_{\text{absorption from a to b}}$$

And $N = N_a + N_b$ (# of atoms).

This rate eqn gives a simple description of out of equilibrium dynamics i.e. if at $t=0$ the system starts with a N_a, N_b distribution different than thermal equilibrium. When $t \to \infty$, we reach a steady state with $\frac{dN_b}{dt} = 0$:

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

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

But from our discussion last week we had $\begin{cases} B_{ba} = \frac{\pi}{3\varepsilon_0 \hbar^2} \left|\vec{P}_{ba}\right|^2 \\ B_{ab} = \frac{\pi}{3\varepsilon_0 \hbar^2} \left|\vec{P}_{ab}\right|^2 \end{cases} \Rightarrow B_{ba} = B_{ab}$

so: $$\rho(\omega_0) = \frac{(A/B_{ba})}{\left(\frac{N_a}{N_b}\right) - 1} = \frac{(A/B_{ba})}{e^{\frac{\hbar\omega_0}{k_B T}} - 1}$$

If we believe in Boltzmann, we must have: $\left(\frac{N_a}{N_b}\right) = e^{-\frac{E_a - E_b}{k_B T}} = e^{\frac{\hbar\omega_0}{k_B T}}$

And if we believe in Planck:

$$\frac{A}{B_{ba}} = \frac{\hbar}{\pi^2 c^3}\omega_0^3 \Rightarrow A = \frac{\cancel{\hbar}}{\pi^{\cancel{2}} c^3}\omega_0^3 \frac{\cancel{\pi}}{3\varepsilon_0 \hbar^{\cancel{2}}} \left|\vec{P}_{ba}\right|^2 = \boxed{\frac{\omega_0^3}{3\pi\varepsilon_0 \hbar c^3} \left|\vec{P}_{ba}\right|^2}.$$

This turns out to be a general result: the spontaneous emission rate from a level i to any level f with $E_i - E_f = \hbar\omega$ is given by:

$$\Gamma_{i\to f}(\omega) = \frac{\omega^3}{3\pi\varepsilon_0 \hbar c^3} \left|\vec{P}_{if}\right|^2 \quad \text{where} \quad \vec{P}_{if} = \langle \psi_i | q\vec{r} | \psi_f \rangle$$

If there are more than one final level:

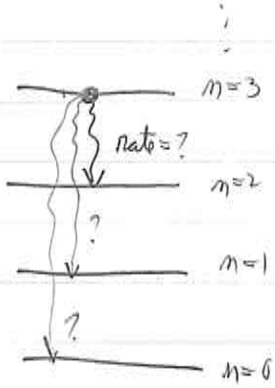
$$\Gamma_{\text{out of } i} = \sum_f \Gamma_{i\to f}$$

And since $\frac{dN_i}{dt} = -N_i \Gamma_{\text{out of } i}$ (assuming no process for replenishing the level):

$$\Rightarrow N_i = N_i(0)\, e^{-\Gamma_{\text{out of } i}\, t}$$ (This is the case for isolated atoms).

Example: Decay rates for harmonic oscillator

In 1d, $H_0 = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega_0^2 x^2$ and $H_0|n\rangle = \hbar\omega_0(n+\frac{1}{2})|n\rangle$, where $n=0,1,2,\dots$



Assume system starts out at state $|n\rangle$. What is the rate for it to spontaneously emit a photon and decay to $|n'\rangle$? ($n'<n$).

The $\Gamma_{i\to f}(\omega) = \frac{\omega^3}{3\pi\varepsilon_0\hbar c^3}\left|\langle i|qx|f\rangle\right|^2$

From $x = \sqrt{\frac{\hbar}{m\omega_0}}\,\frac{(\hat{a}+\hat{a}^\dagger)}{\sqrt{2}}$ we get:

$$\langle n|x|n'\rangle = \sqrt{\frac{\hbar}{2m\omega_0}}\langle n|(\hat{a}+a^\dagger)|n'\rangle = \sqrt{\frac{\hbar}{2m\omega_0}}\langle n|\left(\sqrt{n'}|n'-1\rangle + \sqrt{n'+1}|n'+1\rangle\right)$$

$$= \sqrt{\frac{\hbar}{2m\omega_0}}\left(\sqrt{n'}\,\delta_{n,n'-1} + \sqrt{n'+1}\,\delta_{n,n'+1}\right)$$

$$= \sqrt{\frac{\hbar}{2m\omega_0}}\sqrt{n}\,\delta_{n',n-1} \quad \text{for } n'<n$$

$\Rightarrow$ without [illegible] photons, the only transition that is allowed is from n to $n-1$! All others are zero.

Since $(E_n - E_{n-1}) = \hbar\omega_0$:

$$\Gamma_{n\to n-1} = \Gamma_{i\to f}(\omega=\omega_0) = \frac{\omega_0^3}{3\pi\varepsilon_0\hbar c^3}\left|q\sqrt{\frac{\hbar}{2m\omega_0}}\sqrt{n}\right|^2 = \frac{q^2\omega_0^2}{6\pi\varepsilon_0 c^3 m}\,n$$

The lifetime of the n-th stationary state is:

$$\tau_n = \frac{1}{\Gamma_{n\to n-1}} = \frac{6\pi\,\varepsilon_0\, m\, c^3}{n\, q^2\, \omega_0^2}$$

Power radiated by system in nth state:

$$E_n = \left(n+\tfrac{1}{2}\right)\hbar\omega_0$$

$$P = \underbrace{(\hbar\omega_0)}_{\text{radiated photon}}\,\Gamma_{n\to n-1} = (\hbar\omega_0)\,\frac{q^2\omega_0^2}{6\pi\varepsilon_0 c^3 m}\, n = \frac{q^2\omega_0^2}{6\pi\varepsilon_0 c^3 m}\left(E_n - \frac{\hbar\omega_0}{2}\right)$$

Compare to Classical result (accelerated point charge emitting Em radiation)

$$P_{clas} = \frac{q^2 a^2}{6\pi\varepsilon_0 c^3}$$ where a is the acceleration of point charge q.

For Classical harm. oscillator: $x(t) = x_0 \cos(\omega_0 t) \Rightarrow a = -\omega_0^2 x_0 \cos(\omega_0 t)$

$$\Rightarrow a^2 = \omega_0^4 x_0^2 \underbrace{\langle \cos^2(\omega_0 t)\rangle}_{=\frac{1}{2}}$$

$$\Rightarrow P_{Clas.} = \frac{q^2}{6\pi\varepsilon_0 c^3}\,\omega_0^4 x_0^2 \underbrace{\langle \cos^2(\omega_0 t)\rangle}_{=\frac{1}{2}} = \frac{q^2}{6\pi\varepsilon_0 c^3}\underbrace{\frac{\omega_0^2}{2}\,\frac{2}{m}\overbrace{\left[\frac{1}{2} m\omega_0^2 x_0^2\right]}^{E}}_{\frac{\omega_0^4 x_0^2}{2}} = \frac{q^2\omega_0^2}{6\pi\varepsilon_0 c^3 m}\, E$$

Which is just like the quantum result except for $E \to \left(E - \frac{\hbar\omega_0}{2}\right)$ (quantum result protects ground state from emission). Note how quantum becomes Classical when $\hbar \to 0$.

Selection rules for spontaneous emission of atomic states

Consider a H-atom in the state $\psi_{n\ell m}$. Does the electron stays forever in this state? No! It spontaneously relax towards other states $\psi_{n'm'\ell'}$ by emitting a photon. How to calculate the rate for this transition?

$$\Gamma_{n\ell m \to n'\ell' m'} = \frac{\omega^3 q^2}{3\pi \varepsilon_0 \hbar c^3} \left| \langle \psi_{n\ell m} | \vec{r} | \psi_{n'\ell' m'} \rangle \right|^2$$

where $\omega = \frac{(E_{n\ell m} - E_{n'\ell' m'})}{\hbar}$.

Whether or not $\psi_{n\ell m}$ can decay into $\psi_{n'\ell' m'}$ depends on whether or not

$$\langle \psi_{n\ell m} | \vec{r} | \psi_{n'\ell' m'} \rangle \neq 0 .$$

Selection rules: rules for how the allowed n', ℓ', m' relate to n, ℓ, m.

$\Rightarrow$ Symmetry: $\psi_{n'\ell' m'}$ has to have opposite parity of $\psi_{n\ell m}$.

$\rightarrow$ All selection rules can be derived from symmetry (group theory) using the Wigner-Eckart theorem (Beyond the scope of this course).

Here we will derive them using commutation tricks:

Selection rules involving m and m':

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

$$0 = \langle n'l'm' | [L_z, z] | n l m \rangle = \langle n'l'm' | (L_z z - z L_z) | n l m \rangle$$

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

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

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

$\Rightarrow$ If $m' = m$, a photon with $\vec{E} \parallel \hat{z}$ <u>may</u> be emitted.

For $[L_z, x] = i\hbar y$:

$$\langle n'l'm' | \underbrace{[L_z, x]}_{i\hbar y} | n l m \rangle = i\hbar \langle n'l'm' | y | n l m \rangle$$

$$= (m'\hbar - m\hbar) \langle n'l'm' | x | n l m \rangle$$

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

Similarly, using $[L_z, y] = -i\hbar x$:

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

Combine both ~~results~~:

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

$\Rightarrow$ Either $(m' - m) = \pm 1$ or $\langle n'l'm' | \begin{pmatrix} x \\ y \end{pmatrix} | n l m \rangle = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$.

$\Rightarrow$ If $(m' - m) = \pm 1$ a photon with $\vec{E} \parallel \hat{x} \pm i \hat{y}$ will be emitted ("circularly polarized")

For selection rule for l, note that:

$$\psi_{nlm}(-\vec{r}) = (-1)^l \psi_{nlm}(\vec{r}) \quad \text{(Prove that from spherical harmonics)}.$$

$$\langle \psi_{nlm} | \vec{r} | \psi_{n'l'm'} \rangle = \int d^3r \, \psi_{nlm}(\vec{r}) \, \vec{r} \, \psi_{n'l'm'}(\vec{r})$$

$$\vec{r}' = -\vec{r}$$

$$= -\int d^3r' \, \psi_{nlm}(-\vec{r}') \, \vec{r}' \, \psi_{n'l'm'}(-\vec{r}')$$

$$= -(-1)^{l+l'} \int d^3r' \, \psi_{nlm}(\vec{r}') \, \vec{r}' \, \psi_{n'l'm'}(\vec{r}')$$

$\Rightarrow (l+l')$ has to be odd.

<u>Actually more than that</u>: Use $\left[\hat{L}^2, [\hat{L}^2, \hat{\vec{r}}]\right] = 2\hbar^2 \left(\hat{\vec{r}} \hat{L}^2 + \hat{L}^2 \hat{\vec{r}}\right)$

$$\Rightarrow \langle n'l'm' | [L^2, [L^2, \vec{r}]] | nlm \rangle = 2\hbar^2 \hbar^2 [l(l+1) + l'(l'+1)] \langle n'l'm' | \vec{r} | nlm \rangle$$

$$= \langle n'l'm' | \left(L^2 [L^2, \vec{r}] - [L^2, \vec{r}] L^2 \right) | nlm \rangle = \hbar^2 [l'(l'+1) - l(l+1)] \langle n'l'm' | [L^2, \vec{r}] | nlm \rangle$$

$$= \hbar^2 [l'(l'+1) - l(l+1)] \hbar^2 [l'(l'+1) - l(l+1)] \langle n'l'm' | \vec{r} | nlm \rangle$$

$$\Rightarrow \underbrace{2[l(l+1) + l'(l'+1)]}_{(l'+l+1)^2 + (l'-l)^2 - 1} = \underbrace{[l'(l'+1) - l(l+1)]^2}_{(l'+l+1)(l'-l)} \quad \text{or else } \langle n'l'm' | \vec{r} | nlm \rangle = 0.$$

$$\Rightarrow \left[(l'+l+1)^2 + (l'-l)^2 - 1\right] - (l'+l+1)^2 (l'-l)^2 = 0 \Rightarrow \left[(l'+l+1)^2 - 1\right]\left[1 - (l'-l)^2\right] = 0$$

For 1st factor to be zero we must have: $l' = l = 0$ (remember, l, l' are positive integers)

$\Rightarrow$ from symmetry we know this is not allowed, $l + l'$ would be even.

For 2nd factor to be zero we must have: $l' - l = \pm 1$. This is allowed by symmetry, because $\Delta l = \pm 1$ implies $l + l'$ is odd.

$\Rightarrow \boxed{\Delta l = \pm 1}$

[illegible] transition occurs unless