

## Lecture 37

Last time, considered EM transitions in atoms

Monochromatic light amplitude  $E_0$ :  $P_{\text{abs}} = \left| \frac{\vec{p} \cdot \vec{E}_0}{\hbar} \right|^2 \frac{\sin^2 \frac{\Delta t}{2}}{\Delta^2}$

Incoherent light, spectral density  $\rho$

$$R_{\text{abs}} = \frac{\pi}{3\epsilon_0 \hbar^2} |\vec{p}|^2 \rho(\omega_0)$$

$$\vec{p} = -e\vec{r} = \text{dipole moment operator}$$

Today, tell rest of the story

In particular, discuss spontaneous emission

Atom in excited state, say 2p state of H  
can spontaneously decay to a lower energy state

This should be surprising...

2p state is an eigenstate

- If we don't apply a perturbation, state shouldn't change

Why does it?

Need to develop quantum theory of EM field to answer.

That takes some work, Griffiths doesn't cover it

So I'll just give the idea

Say atom was in a box with perfectly conducting walls.

Then only certain modes of EM field allowed

$$\vec{E}(\vec{r}, t) = A \hat{e} \sin \frac{n_x \pi x}{L_x} \sin \frac{n_y \pi y}{L_y} \sin \frac{n_z \pi z}{L_z} \cos \omega t$$

$$\vec{k} = \pi \left( \frac{n_x}{L_x}, \frac{n_y}{L_y}, \frac{n_z}{L_z} \right) \quad \omega = \frac{|\vec{k}|}{c}$$

Just like particle in a box!

Consider a single mode  $(n_x, n_y, n_z)$

$$\begin{aligned} \text{Energy of mode} &= \int u d^3r & u(\vec{r}) &= \frac{1}{2\epsilon_0} |\vec{E}(\vec{r})|^2 \\ &= \frac{1}{2\epsilon_0} \frac{V}{8} \end{aligned}$$

In quantum EM, amplitude  $A$  itself becomes quantum variable

$$\text{Hamiltonian } H = \frac{V}{16\epsilon_0} |A|^2$$

Actually need to let  $A$  be complex

$$\text{if } A = |A| e^{i\phi}, \quad E \propto |A| \cos(\omega t + \phi) \\ = \text{Re}[A e^{i\omega t}]$$

Use same trick in classical optics, if you've seen it

Say  $A = q + ip$ ,  $q, p$  both  $\rightarrow$  quantum operators

$$\text{Then } H = \frac{V}{16\epsilon_0} (q^2 + p^2)$$

Just like Hamiltonian for harmonic oscillator

⇒ Each mode of field acts just like quantum harmonic oscillator

Allowed energies  $E = \hbar\omega(n + \frac{1}{2})$   
 ⇒ photons

Get all kind of interesting things, but what I wanted to point out is zero point energy:  $\frac{\hbar\omega}{2}$

Corresponds to non-zero zero-point field  $E_0$

So even in empty box w/ no photons, still have quantum electric field noise.

It turns out, this noise can drive atomic transitions.

Only from excited state → lower state  
 (atom can emit energy into field, can't absorb any)

Called spontaneous emission

Can see how it works

$$\text{Have } R = \frac{\pi}{3\epsilon_0 \hbar^2} |\vec{p}|^2 \rho(\omega_0)$$

$$\text{Here } \rho(\omega_0) = \frac{\frac{1}{2}\hbar\omega_0}{V} \times (\# \text{ of states between } \omega_0 \text{ and } \omega_0 + d\omega)$$

Work out just as for electrons in a box

$$= \frac{V}{\pi^2 c^3} \omega_0^2$$

$$R_{sp} = \frac{\pi}{3\epsilon_0 \hbar^2} |\vec{p}|^2 \cdot \frac{\hbar \omega_0}{2V} \cdot \frac{V}{\pi^2 c^3} \omega_0^2$$

$$= \frac{1}{6\pi\epsilon_0} |\vec{p}|^2 \frac{\omega_0^3}{\hbar c^3}$$

Turns out, real answer is twice this

$$R_{sp} = \frac{1}{3\pi\epsilon_0 \hbar} |\vec{p}|^2 \left(\frac{\omega_0}{c}\right)^3$$

Hard-waving can only get you so far in life...

To do correctly, either develop quantum EM for real,  
or can get from statistical argument (section 9.3)

So generally, two ways to drive a transition

Stimulated: apply a field, it drives  $\psi_a \leftrightarrow \psi_b$   
(reversible)

Spontaneous: "vacuum" field drives  $\psi_b \rightarrow \psi_a$   
(irreversible)

Problem first considered by Einstein

Sometimes still see his notation

Write  $R_{sp} = A =$  Einstein A coefficient

$R_{stim} = B\rho(\omega_0)$ , Einstein B coefficient

$$\text{So } A = \frac{|\vec{p}|^2 \omega_0^3}{3\pi\epsilon_0 \hbar c^3}$$

$$B = \frac{\pi |\vec{p}|^2}{3\epsilon_0 \hbar^2}$$

So lets say we have a collection of atoms

$\mathcal{Z}_e =$  ground state

$\mathcal{Z}_s =$  excited state

We apply radiation with given  $\rho(\omega_0)$

Can solve for state populations very easily

Say  $N_e$  atoms in  $\mathcal{Z}_e$

$N_s$  in  $\mathcal{Z}_s$

$N = N_e + N_s$  total

$$\frac{dN_s}{dt} = \underbrace{-AN_s}_{\substack{\uparrow \\ \text{spontaneous} \\ \text{emission}}} - \underbrace{BN_s\rho(\omega_0)}_{\substack{\uparrow \\ \text{stim} \\ \text{emission}}} + \underbrace{BN_e\rho(\omega_0)}_{\substack{\uparrow \\ \text{stim} \\ \text{absorption}}}$$

In equilibrium,  $\frac{dN_s}{dt} = 0$

also  $N_e = N - N_s$

$$\text{Then } -AN_s - BN_s\rho + BN\rho - BN_s\rho = 0$$

$$N_s(A + 2B\rho) = NB\rho$$

$$\boxed{\frac{N_s}{N} = \frac{B\rho}{A + 2B\rho}}$$

Gives population in excited state as function of  $\rho$

Note, this only works for incoherent radiation

monochromatic radiation gives Rabi oscillations,

more complicated with spontaneous emission

Finally, spontaneous emission sets lifetime of excited state

If  $\rho = 0$ , no applied field,

$$\frac{dN_2}{dt} = -AN_2 \Rightarrow N_2(t) = N_2(0)e^{-At}$$

Exponential decay, "lifetime"  $\tau = \frac{1}{A} = \frac{3\pi\epsilon_0\hbar c^3}{17\pi^2\omega_0^3}$

For instance, lifetime of  $2_{210}$  state of hydrogen

Have  $\gamma_2 = -e\langle 2_{210} | z | 2_{100} \rangle$   
 $= -ea \left( \frac{2^{15/2}}{3^5} \right)$  from last time

For this state,  $\gamma_x = \gamma_y = 0$  ( $2_{210}$  &  $2_{100}$  indep of  $\phi$ )

$$|\vec{\gamma}|^2 = \gamma_z^2 = e^2 a^2 \frac{2^{15}}{3^{10}}$$

$$\tau = \frac{3\pi\epsilon_0\hbar c^3}{\omega_0^3} \cdot \frac{3^{10}}{2^{15}} \frac{1}{e^2 a^2}$$

$$\omega_0 = \frac{1}{\hbar} (E_2 - E_1) = \frac{1}{\hbar} (-E_1) \left( 1 - \frac{1}{4} \right)$$

$$= -\frac{E_1}{\hbar} \frac{3}{4}$$

$$\tau = \frac{3^{11}}{2^{15}} \pi \left( \frac{4}{3} \right)^3 \frac{\epsilon_0 \hbar^4 c^3}{(-E_1)^3} \frac{1}{e^2 a^2}$$

Use  $\frac{e^2}{4\pi\epsilon_0} = \hbar c \alpha$

$$a = \frac{\hbar}{m c \alpha}$$

Get  $\tau = \frac{3^8}{2^9} \frac{1}{\alpha^3} \frac{\hbar}{(-E_1)}$

$$E_1 = -\frac{\alpha^2 m c^2}{2}$$

$$\frac{\hbar}{-E_1} = 2 \cdot 10^{16} \text{ s}^{-1}$$

$$\alpha = \frac{1}{137}$$

$$S_0 \quad \tau = 1.6 \times 10^{-9} \text{ s}$$

Get some answer for other  $2p$  states

Note, this means energy of  $2p$  state is intrinsically uncertain:

$$\Delta E \approx \frac{\hbar}{\tau} = 4 \times 10^{-7} \text{ eV}$$

$$\frac{\Delta E}{h} = 100 \text{ MHz}$$