Lecture 28

Last time, introduced idea of spontaneous emission
QM system in excited state will decay to
ground state

Driven by "zero-point" quantum EM field

Get rate from Einstein:
If incoherent radiation drives transition
at rate
\[
R_{\text{stim}} = \frac{\beta}{\rho(\omega_0)}
\]

Then spontaneous emission occurs at
rate
\[
R_{\text{spont}} = A = \frac{\epsilon^2 \omega_0}{\pi^2 c^3} \beta
\]
\[
= \frac{8\pi^2}{\lambda^3} \beta
\]

In dipole approximation, \( \beta = \frac{\pi}{36\epsilon_0 k^2} |\vec{\gamma}|^2 \)

so
\[
A = \frac{\omega_0^2 |\vec{\gamma}|^2}{3\pi\epsilon_0 k c^3}
\]

In modern use, typically write \( \Gamma \) instead of \( A \)

For hydrogen, can calculate \( |\vec{\gamma}|^2 \rightarrow A \) exactly

For other atoms, very difficult. Typically

\underline{measure} \( A \) (= 1/lifetime of state)
and get \( |\vec{\gamma}|^2 \) from that

For instance, in Rb atoms, lowest excited state is \( 5P \)
decays to \( 5S \)
Lifetime of $5p = 26.6$ ns

\[ \lambda \approx 1 \text{ au} \approx 3 \text{ mm} \]

Always $\approx \text{ea}$ for dipole allowed transitions.

\[ \Phi = \langle b| e^2 |a \rangle \neq 0 \]

In many cases, $\Phi = 0$. For instance, if both $2s$ and $2p$ are s-states, then $\Phi = 0$ by symmetry.

In such cases, transitions are much slower.

- Driven by
  1. Higher-order electric field
     \[ \text{in Taylor expansion of } \cos(\vec{k} \cdot \vec{r} - \omega t) \]
     \[ \Rightarrow \text{problem 9.21} \]
  2. Magnetic part of E-M field
     Smaller by $\frac{1}{c}$
  3. Multi-photon process
     \[ \text{ie, emit two photons } \omega_1 + \omega_2 \text{ with } \]
     \[ \omega_1 + \omega_2 = \omega_0 \]

Generally much slower.

Lifetime of $2s$ state in hydrogen $= 0.15$ ns

(US $1.6$ ns for $2p$)
Important to know what transitions are, dipole-allowed
Described by "selection rules"

Rules for when \( \langle n' l' m' | \hat{L}_z | n l m \rangle \neq 0 \)

Get two rules
1. Require \( \Delta m = 0, \pm 1 \)
2. Require \( \Delta l = \pm 1 \)

Prove using commutators

Consider \( \left[ \hat{L}_z, x \right] = \left[ x \rho_y - y \rho_x, x \right] \)

\( = \left[ x \rho_y, x \right] - \left[ y \rho_x, x \right] \)

\( = -\left[ y \rho_x, x \right] \)

\( = -y \left[ \rho_x, x \right] \)

\( = -y (-ix) \)

\( = ixy \)

Similarly, \( \left[ \hat{L}_z, y \right] = -ix \)

\( \left[ \hat{L}_z, z \right] = 0 \)

Then
\( 0 = \langle n' l' m' | \left[ \hat{L}_z, z \right] | n l m \rangle = \mp \langle n' l' m' | (m' - m) z | n l m \rangle \)

\( \Rightarrow \rho_z = 0 \) unless \( m = m' \Rightarrow \Delta m = 0 \)
with $[L_z, y] \Rightarrow$

\[
\langle 2'1 L_z x \cdot -x L_z \mid 2' \rangle = (m'-m) \mp \langle 2'1 \rangle \hat{1} 14' \rangle \\
= i \mp \langle 2'1 \rangle \hat{1} 14' \rangle \\
= \rangle \rightarrow \langle \psi \rangle = -i (m'-m) \langle \psi \rangle
\]

Similarly $[L_z, y] \Rightarrow$

\[
\langle \psi \rangle = -i (m'-m) \langle \psi \rangle
\]

So
\[
\langle \psi \rangle \langle \psi \rangle = (m'-m)^2 \langle \psi \rangle \langle \psi \rangle
\]

\[
\Rightarrow \text{either } (m'-m)^2 = 1 \text{ or } \langle \psi \rangle \langle \psi \rangle = 0
\]

\[
\Rightarrow \Delta m = \pm 1
\]

So all together, need $\Delta m = 0, \pm 1$

For 2nd rule, need complicated commutator

\[
[\hat{L}^2, [\hat{L}^2, \hat{\psi}]] = 2z^2 \hat{\psi} \hat{L}^2 + L^2 \hat{\psi}
\]

(vector, holds independently for $x, y, z$)

Seen will present

Implies

\[
\langle 2'1 \mid [\hat{L}^2, [\hat{L}^2, \hat{\psi}]] \mid 2' \rangle = 2z^2 \langle 2'1 \hat{\psi} \hat{L}^2 + L^2 \hat{\psi} \rangle \\
= 2z^4 [\hat{L}(\hat{L}+1) + z'(\hat{L}+1)] \langle 2'1 \rangle Evaluation
while $\langle\phi_1\mid \mathcal{L}_z^2, (\mathcal{L}_x^2, \mathcal{L}_y^2) \rangle_{14}$

$= \langle\phi_1\mid \mathcal{L}_x^2 \mathcal{L}_z^2 \phi_1 \rangle - \langle\phi_1\mid \mathcal{L}_x^2 \mathcal{L}_z^2 \phi_1 \rangle_{14}$

$= \frac{\hbar^2}{2} [l'(l'+1) - l(l+1)] \langle\phi_1\mid \mathcal{L}_x^2 \phi_1 \rangle - \frac{\hbar^2}{2} \langle\phi_1\mid \mathcal{L}_z^2 \phi_1 \rangle_{14}$

$= \frac{\hbar^2}{2} [l'(l'+1) - l(l+1)]^2 \langle\phi_1\mid \mathcal{L}_z^2 \phi_1 \rangle_{14}$

Together, require $2 [l'(l'+1) + l'(l'+1)] = [l'(l'+1) - l(l+1)]^2$

Not so easy to solve a quartic equation.

But turns out it factors into two quadratics

$[l'(l'+1)^2 - 1] [l(l+1)^2 - 1] = 0$

So either $(l'+l+1)^2 = 1$

$\Rightarrow l' = l = 0$, but we know $\phi_0 = 0$ in that case already.

Or, $(l' - l)^2 = 1 \Rightarrow l' = l \pm 1$

\[\Delta l = \pm 1\] as claimed.

Note, this can be derived more easily with some fancier math (group theory).

Also can see that need $\Delta l = \text{odd}$ pretty easily.

Since $2n_m = \text{even}$ for $l$ even

and $\phi_m = \text{odd}$ for $l$ odd
\[
\left[ 6 \times - 2 \times \frac{1}{2} \right] + 2 = \left( \frac{8}{2} \right)
\]

\[
\left[ x \times 4 \times \frac{1}{3} - \frac{9}{2} \times 2 \right] + \frac{2}{3} = \left[ x \times \left( \frac{1}{3} \right) - \frac{8}{3} \right]
\]

\[
0 = \left[ \frac{8}{3} \right] = \left[ \frac{8}{3} \right]
\]

\[
\left[ \frac{1}{3} \times \frac{1}{4} \right] - \left[ \frac{1}{4} \times \frac{1}{4} \right] - \left[ \frac{1}{4} \times \frac{1}{4} \right] = \frac{1}{3} \times \left( \frac{1}{4} \right)
\]

\[
\left[ \frac{1}{3} \times \frac{1}{4} \right] + \left[ \frac{1}{3} \times \frac{1}{4} \right] - \frac{1}{3} \times \left( \frac{1}{4} \right)
\]

\[
\left[ \frac{1}{3} \times \frac{1}{4} \right] + \left[ \frac{1}{3} \times \frac{1}{4} \right] - \frac{1}{3} \times \left( \frac{1}{4} \right)
\]

\[
\left[ \frac{1}{3} \times \frac{1}{4} \right] + \left[ \frac{1}{3} \times \frac{1}{4} \right] - \frac{1}{3} \times \left( \frac{1}{4} \right)
\]

\[
\frac{1}{3} \times \left( \frac{1}{4} \right) + \left( \frac{1}{4} \right) \frac{1}{3} + \frac{1}{3} \left( \frac{1}{4} \right) - \left( \frac{1}{4} \right) \frac{1}{3} = \frac{1}{3} \frac{1}{4} + \left( \frac{1}{4} \right) \frac{1}{3} + \frac{1}{3} \left( \frac{1}{4} \right) - \left( \frac{1}{4} \right) \frac{1}{3}
\]

\[
0 + \frac{3}{4} \left[ \frac{2}{3} \right] + \left[ \frac{2}{3} \right] + \frac{1}{3} \left[ \frac{2}{3} \right] + \left[ \frac{2}{3} \right] = \left( \frac{2}{3} \right)
\]
So \[ [L^2, [L^2, z]] = -2 t^2 \sum \left( \frac{1}{2} \int \frac{1}{2} x L_x L_y - 2 \frac{1}{2} \frac{i}{2} x L_y + 2 \frac{1}{2} \frac{i}{2} x L_x \right) \]

\[ = -2 t^2 \left( \frac{1}{2} \int \frac{1}{2} x L_x L_y - 2 \frac{1}{2} \frac{i}{2} x L_y + 2 \frac{1}{2} \frac{i}{2} x L_x \right) \]

\[ = 2 t^2 \left( L_x^2 + 2 L_y^2 \right) - 4 t^2 \left( L_x^2 - \frac{1}{2} L_y + \frac{1}{2} L_x \right) \]

\[ = 2 t^2 \left( L_x^2 + 2 L_y^2 \right) - 4 t^2 \left( \frac{1}{2} L_x L_y + L_x L_y + \frac{1}{2} L_x^2 \right) \]

\[ \left[ L_x, \left( \frac{1}{2} \cdot L \right) \right] \]

\[ \frac{1}{2} \cdot L = \frac{1}{2} \cdot \left( x y \right) = 0 \]

So \[ [L^2, [L^2, z]] = 2 t^2 \left( L_x^2 + 2 L_y^2 \right) \] as required.