Lecture 36

Continuing with time dependent PT

For sinusoidal driving field, have

$$P_{a\to b}(t) \approx \frac{|V_{ab}|^2}{\hbar^2}\,\frac{\sin^2\frac{\Delta t}{2}}{\Delta^2} \qquad \Delta = \omega-\omega_0$$

for any system, as long as $P_{max} \ll 1$

Or $P_{a\to b}(t) = \frac{|V_{ab}|^2}{\hbar^2\Delta^2+|V_{ab}|^2}\sin^2\omega_r t$ for two-level system, $|V_{ab}|, |\Delta| \ll \hbar\omega_0$

and

$$\omega_r = \frac{1}{2}\sqrt{\Delta^2+\frac{|V_{ab}|^2}{\hbar^2}}$$

Today, consider specifically driving transitions in atoms with an E&M field.

H^0 = atomic Hamiltonian (Hydrogen)

H' = energy of electron in E+M field

Neglecting B-field for now, = energy in E-field

$H' = -e\phi$ $\qquad \phi$ = electric potential $= -\int \vec{E}\cdot d\vec{r}$

Say $\vec{E} = E_0\hat{z}\cos(ky-\omega t)$: plane wave polarized along z, travelling along y $\quad k = \frac{\omega}{c} = \frac{2\pi}{\lambda}$

Then $\phi = -E_0 z\cos(ky-\omega t)$

$H' = eE_0 z\cos(ky-\omega t)$

We need $H'_{ba} = eE_0 \langle \psi_b | z \cos(ky - \omega t) | \psi_a \rangle$

Now, electron in atom is localized to $\sim a$
$\approx 5 \times 10^{-11}$ m

$\cos ky$ varies over length $\frac{1}{k} \approx \lambda$
For visible light, $\lambda \sim 5 \times 10^{-7}$ m $\gg a$

So spatial variation of cosine is not significant
Approximate $y \to y_0$ = location of atom
for simplicity, take $y_0 = 0$

Then $H'_{ba} \to eE_0 \cos\omega t \langle \psi_b | z | \psi_a \rangle$

Define $\wp = \langle \psi_b | (-ez) | \psi_a \rangle$
= matrix element of dipole moment

"dipole approximation"

$\vec{p} = q\vec{r}$

$H'_{ba} = -\wp E_0 \cos\omega t$ like before, $V_{ba} = -\wp E_0$

So we get
$$P_{a\to b} = \left| \frac{\wp E_0}{\hbar} \right|^2 \frac{\sin^2 \Delta t/2}{\Delta^2}$$
in perturbative limit.

That is very handy if you are driving transition using a laser.

However, very often you don't have a laser,
you have light from a lamp (or the sun, or a flare, etc.)

Then we don't have one well defined ω,
we have a whole range

Call such illumination <u>incoherent</u>

Hard to write down E, instead use energy density:

For monochromatic light, $u = \frac{\epsilon_0}{2} E_0^2$ $u\,d^3r$ = energy in volume d^3r

See $P_{abs} = \frac{2u}{\epsilon_0 \hbar^2} |\wp|^2 \frac{\sin^2 \Delta t/2}{\Delta^2}$

For incoherent light,

$$u \to \int \rho(\omega)\, d\omega$$

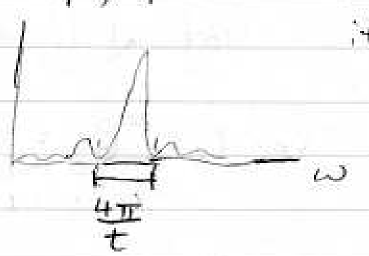
$\rho(\omega)$ = spectral energy density

$\rho(\omega)\, d\omega\, d^3r$ = energy in volume d^3r with freq between ω & $\omega + d\omega$

Each increment $d\omega$ contributes to P, so

$$P_{abs} \to \frac{2}{\epsilon_0 \hbar^2} |\wp|^2 \int \rho(\omega) \frac{\sin^2 \frac{(\omega-\omega_0)t}{2}}{(\omega-\omega_0)^2}\, d\omega$$

Now $\frac{\sin^2 \frac{(\omega-\omega_0)t}{2}}{(\omega-\omega_0)^2}$ is sharply peaked at $\omega = \omega_0$ if $\omega t \gg 1$



So only values of ρ near ω_0 will be important; approximate ρ as constant:

$$P \approx \frac{2}{\epsilon_0 \hbar^2} |\wp|^2 \rho(\omega_0) \int \frac{\sin^2 \frac{\Delta t}{2}}{\Delta^2}\, d\Delta$$

Change variables $v = \frac{\Delta t}{2}$ $dv = \frac{t}{2}$

Then
$$P = \frac{2}{\varepsilon_0 \hbar^2} |\wp|^2 \rho(\omega_0) \frac{t}{2} \int_{-\infty}^{\infty} \frac{\sin^2 v}{v^2} dv$$

Look up definite integral $= \pi$

So $P = \frac{\pi}{\varepsilon_0 \hbar^2} |\wp|^2 \rho(\omega_0) t$

Grows linearly in time

Note, in monochrometic formula with $\Delta = 0$,
P grows quadratically in time

Here linear, because for longer times a narrower
range of ω contributes

Typically define transition rate

$$R = \frac{dP}{dt} = \frac{\pi}{\varepsilon_0 \hbar^2} |\wp|^2 \rho(\omega_0)$$

Polarization effects:
We've assumed light is polarized along z.
Natural light typically unpolarized.

Really $R_z = \frac{\pi}{\varepsilon_0 \hbar^2} |\wp_z|^2 \rho_z(\omega_0)$

= transition rate for z
polarized light

$\wp_z$ = z comp of dipole moment
ρ_z = density of z polarized light

Get same form for y & z polarizations.

By symmetry, $|\wp_z|^2 = |\wp_x|^2 = |\wp_y|^2$ (atoms have no preferred direction)

often write $|\vec{\wp}|^2 = |\wp_x|^2 + |\wp_y|^2 + |\wp_z|^2 = 3|\wp_z|^2$

Then

$$R_i = \frac{\pi}{3\varepsilon_0 \hbar^2} |\vec{\wp}|^2 \rho_i(\omega_0) \qquad (i^{th} \text{ component})$$

Total rate $R = \sum R_i = \frac{\pi}{3\varepsilon_0 \hbar^2} |\vec{\wp}|^2 \sum \rho_i(\omega_0)$

$$\boxed{R = \frac{\pi}{3\varepsilon_0 \hbar^2} |\vec{\wp}|^2 \rho(\omega_0)}$$

for $\rho = \sum \rho_i$ = total energy density

(Griffith's makes this much more complicated than it is.)

For an example of calculating $\vec{\wp}$, consider Problem 9.1

Calculate $\langle i | ez | j \rangle$ between ground state $n=1$ & excited states $n=2$

Ignore spin:
- H' doesn't couple to spin directly
- Spin-orbit coupling would actually change what excited states are, but averages out to same overall effect.

So ground state = 1s
excited states 2s, 2p with $m = 0, \pm 1$

$\langle 200 | z | 100 \rangle = 0$, since ψ_{1s} & ψ_{2s} are even in z

$\langle 211 | z | 100 \rangle = \int R_{21}(r)^* \, Y_1^1(\theta,\phi)^* \, z \, R_{10}(r) \, Y_0^0(\theta,\phi) \, d^3r$

But $z = r\cos\theta$, no ϕ dependence
$Y_0^0 = \frac{1}{\sqrt{4\pi}}$, "

$Y_1^1 \propto e^{i\phi}$

So ϕ integral $= \int_0^{2\pi} e^{-i\phi} \, d\phi = 0$

Similarly $\langle 21\,-1 | z | 100 \rangle = 0$

Then
$\langle 210 | z | 100 \rangle = \int R_{21}(r)^* \, Y_1^0(\theta,\phi)^* \, z \, R_{10}(r) \, Y_0^0(\theta,\phi) \, d^3r$

$R_{10}(r) = \frac{2}{a^{3/2}} e^{-r/a}$

$z = r\cos\theta$ $\qquad R_{21}(r) = \frac{1}{\sqrt{24}} \frac{1}{a^{3/2}} \frac{r}{a} e^{-r/2a}$

$Y_0^0 = \frac{1}{\sqrt{4\pi}} \qquad Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos\theta$

Nice to break into radial part and angular part

Angular part: $\frac{\sqrt{3}}{4\pi} \int_0^{\pi} \cos^2\theta \sin\theta \, d\theta \int_0^{2\pi} d\phi$

$= \frac{\sqrt{3}}{2} \left. -\frac{\cos^3\theta}{3} \right|_0^{\pi}$

$= \frac{\sqrt{3}}{2} \times \frac{2}{3} = \frac{1}{\sqrt{3}}$

Radial part

$$\frac{1}{\sqrt{6}} \frac{1}{a^3} \int_0^\infty \left(\frac{r}{a} e^{-r/2a}\right)\left(e^{-r/a}\right)(r)\, r^2 dr$$

$$= \frac{1}{\sqrt{6}} \frac{1}{a^4} \int_0^\infty r^4 e^{-\frac{3}{2}\frac{r}{a}} dr$$

$$= \frac{1}{\sqrt{6}} \frac{1}{a^4} 4! \left(\frac{2a}{3}\right)^5$$

$$= 4 \cdot \sqrt{6}\, a \left(\frac{2}{3}\right)^5$$

So $\langle 210 | z | 100 \rangle = 4 \cdot \sqrt{2} \left(\frac{2}{3}\right)^5 a$

$$= \frac{2^{15/2}}{3^5} a = 0.745a$$