Time Dependent Perturbation Theory

Main application: Absorption / Emission of radiation from atom.

$$\hat{H} = \hat{H}_0 + \lambda \hat{V}(t)$$

this a "real" time dependence

$\underline{\text{not}}$ Heisenberg picture $e^{iH_0 t} \hat{V} e^{-iH_0 t}$

Assume we understand $\hat{H}_0$ part

$$\hat{H}_0 \phi_n = E_n \phi_n \qquad E_n = \hbar \omega_n$$

$$\phi_n(\vec{r}, t) = e^{-i\omega_n t} \phi_n(r)$$

We know how to solve $\lambda = 0$

$$\psi(\vec{r}, t=0) = \sum c_n \phi_n(\vec{r}) \qquad c_n = \langle \phi_n | \psi_n(\vec{r}, t=0) \rangle$$

$$\psi(\vec{r}, t) = \sum c_n e^{-i\omega_n t} \phi_n(\vec{r})$$

For $\lambda \neq 0$ Let's write

$$\psi(r,t) = \sum_n c_n(t)\, \psi_n(r,t)$$

$$i\hbar \frac{d\psi}{dt} = (\hat{H}_0 + \lambda \hat{V})\,\psi$$

$$i\hbar \sum_n \dot{c}_n e^{-i\omega_n t} \phi_n + \sum_n c_n E_n e^{-i\omega_n t} \phi_n$$

$$= \sum_n c_n E_n e^{-i\omega_n t} \phi_n + \sum_n c_n e^{-i\omega_n t} \lambda \hat{V} \phi_n$$

Take inner product with ϕ_k

$$\Rightarrow \quad i\hbar \dot{c}_k = \lambda \sum_n \langle k|\hat{V}|n\rangle c_n$$

Expand $\quad c_k = c_{k0} + \lambda c_{k1} + \lambda^2 c_{k2}$

$$i\hbar \dot{c}_{k0} = \emptyset \qquad \leftarrow \text{expected!}$$

$$i\hbar \dot{c}_{k1} = \sum_n \langle k|V|n\rangle c_{n0}$$

NB $\quad |n\rangle \to \psi_n = e^{-i\omega_n t}\phi_n$ has its time dep.

$\vdots$

Let's suppose system starts in definite state ϕ_ℓ

at $t = -\infty$ so that $c_{n0}(-\infty) = \delta_{n\ell}$

$$i\hbar \dot{c}_{k_1}(t) = \langle k|V|l\rangle$$

$$c_{k_1}(t) = \frac{1}{i\hbar}\int_{-\infty}^{t} \langle k|\hat{V}(t')|l\rangle \, dt'$$

Often $\hat{V}$ is "factorable" ie $\hat{V}$ looks like some operators $(\hat{x}, \hat{p}, \hat{L}, \ldots)$ multiplied by some scalar $f(t)$. Eg time dependent Electric field in $\hat{z}$ direction $\hat{V} = -e\mathcal{E}z\, f(t)$

$$\hat{V} = \hat{\vartheta} f(t)$$

$$c_{k_1}(t) = \frac{\langle k|\hat{\vartheta}|l\rangle}{i\hbar}\int_{-\infty}^{t} e^{i\omega_k t'} e^{-i\omega_l t'} f(t')\, dt'$$

$$P_{l\to k} = |c_{k_1}(t)|^2 = \frac{|\langle k|\hat{\vartheta}|l\rangle|^2}{\hbar^2}\left|\int_{-\infty}^{t} e^{i(\omega_k-\omega_l)t'} f(t')\,dt'\right|^2$$

Physically reasonable ; Probability of transition : (1) $\hat{\vartheta}$ must "connect" l to k. (2) $f(t)$ must have fourier component at correct energy difference

"QM analog of resonance"

Let's specialize to sinusoidal perturbation which is turned on at $t=0$.

$$\hat{V}(t) = \hat{\vartheta}\cos\omega t$$

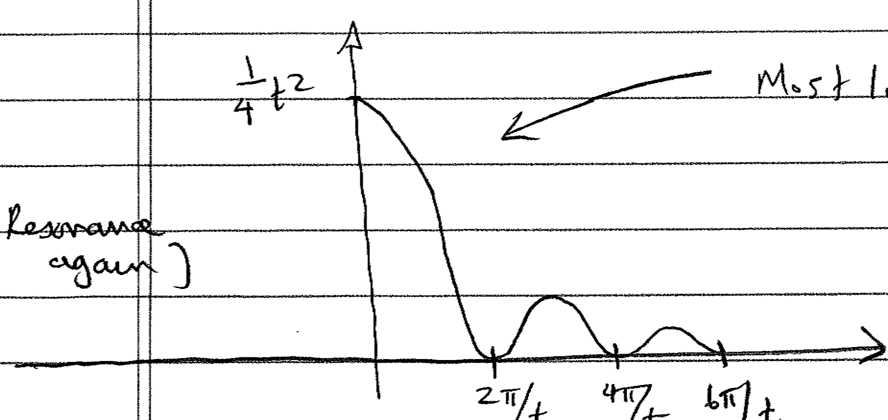
$$c_{k_1}(t) = \frac{\langle k|\hat{\vartheta}|\ell\rangle}{i\hbar}\int_0^t e^{i\omega_{k\ell}t'}\cos\omega t'\,dt'$$

$$= \frac{\langle k|\hat{\vartheta}|\ell\rangle}{2i\hbar}\left[\underbrace{\frac{e^{i(\omega_{k\ell}+\omega)t}-1}{\omega_{k\ell}+\omega}}_{\text{discard}} + \frac{e^{i(\omega_{k\ell}-\omega)t}-1}{\omega_{k\ell}-\omega}\right]$$

Consider ω close to $\omega_{k\ell}$

$$c_{k_1}(t) = \frac{\langle k|\hat{\vartheta}|\ell\rangle}{2i\hbar}\,\frac{e^{i(\omega_{k\ell}-\omega)t/2}}{\omega_{k\ell}-\omega}\left[e^{i(\omega_{k\ell}-\omega)t/2} - e^{-i(\ \ )t/2}\right]$$

$$\boxed{P_{\ell\to k} = \frac{|\langle k|\hat{\vartheta}|\ell\rangle|^2}{\hbar^2}\,\frac{\sin^2(\omega_{k\ell}-\omega)t/2}{(\omega_{k\ell}-\omega)^2}}$$



[Resonance again]

Most likely to excite $\omega_{k\ell}=\omega$

Longer $t \Rightarrow$ more narrow resonance

$\Delta E \Delta t$

uncertainty reln.

In fact $\delta(\omega) = \lim_{t \to 0} \frac{\sin^2(\omega t/2)}{t\omega^2}$

So that $P_{\ell \to k} = \frac{2\pi t}{\hbar^2} |\langle k|\hat{V}|\ell\rangle|^2 \delta(\omega_{k\ell} - \omega)$

$$\boxed{\text{transition rate} \quad w_{\ell \to k} = \frac{P_{\ell \to k}}{t} = \frac{2\pi}{\hbar^2} |\langle k|\hat{V}|\ell\rangle|^2 \delta(\omega_{k\ell} - \omega)}$$

Q: Does anyone know what this is called?

"Fermi's Golden Rule"

Also sometimes formulated in terms of "density of states"

$$w_{\ell \to k} = \frac{2\pi}{\hbar} |\langle k|\hat{V}|\ell\rangle|^2 \, g(E_k)$$

# of states with energy E_k

We discussed keeping only the term

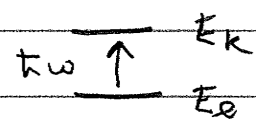
$$\frac{e^{i(\omega_{k\ell}-\omega)t}-1}{\omega_{k\ell}-\omega}$$

and discarding $$\frac{e^{i(\omega_{k\ell}+\omega)t}-1}{\omega_{k\ell}+\omega}$$

The correct thing to say is that <u>both</u> terms are present

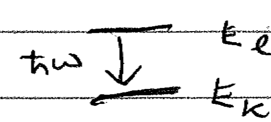
The one we retained corresponds to $E_k = E_\ell + \hbar\omega$

absorption of a photon



The other to emission of a photon

$E_k = E_\ell - \hbar\omega$



One refers to this as "stimulated emission"

A photon in the perturbing field of frequency ω

<u>encourages</u> an atom in an excited state to emit

another photon of same ω!

Stimulated emission first predicted by Einstein

Actually this is fundamental principle behind laser

light amplification by stimulated emission of radiation

Need population inversion for this to occur.

Q: Does this all mean atom in excited state with **NO** external field would never decay?

might think answer "yes" because eigenstate only evolves by trivial phase

A: No. Can have spontaneous emission

Even Vacuum has fluctuating $\vec{E}, \vec{B}$ fields.
(like harmonic oscillator which has ground state energy)

Consider atom exposed to $\vec{E} = E_0 \cos\omega t \, \hat{z}$

$$\hat{V} = -q E_0 \cos\omega t \, \hat{z} \qquad (q = -e)$$

The relevant matrix element is $\langle k | \hat{z} | l \rangle$

or, in general $\langle k | \vec{r} | l \rangle$

Many of these are zero "Selection Rules"

More precisely, for atom $\langle n' l' m' | \vec{r} | n l m \rangle$

$$[\hat{L}_z, \hat{x}] = [\hat{x}\hat{p}_y - \hat{y}\hat{p}_x, \hat{x}] = -[\hat{y}\hat{p}_x, \hat{x}]$$

$$= -\hat{y}[\hat{p}_x, \hat{x}] - [\hat{y}, \hat{x}]\hat{p}_x = i\hbar \hat{y}$$

$$[\hat{L}_z, \hat{y}] = -i\hbar \hat{x} \qquad [\hat{L}_z, \hat{z}] = \phi$$

$$\phi = \langle n' l' m' | [\hat{L}_z, \hat{z}] | n l m \rangle$$

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

$\Rightarrow$ $m' = m$ or $\langle n' l' m' | \hat{z} | n l m \rangle = \phi$.

$$\langle n' l' m' | [\hat{L}_z, \hat{x}] | n l m \rangle = (m' - m)\hbar \langle n' l' m' | \hat{x} | n l m \rangle$$

$$= i\hbar \langle n' l' m' | \hat{y} | n l m \rangle$$

So M.E. of $\hat{y}$ obtained from $\hat{x}$,

$$\langle n'\ell'm'|[\hat{L}_z,\hat{y}]|n\ell m\rangle = (m'-m)\hbar\langle n'\ell'm'|\hat{y}|n\ell m\rangle$$

$$= -i\hbar\langle n'\ell'm'|\hat{x}|n\ell m\rangle$$

combining $(m'-m)^2\langle n'\ell'm'|\hat{x}|n\ell m\rangle$

$$= \langle n'\ell'm'|\hat{x}|n\ell m\rangle$$

so $\langle n'\ell'm'|\hat{x}|n\ell m\rangle = 0$ or $(m'-m)^2 = 1$

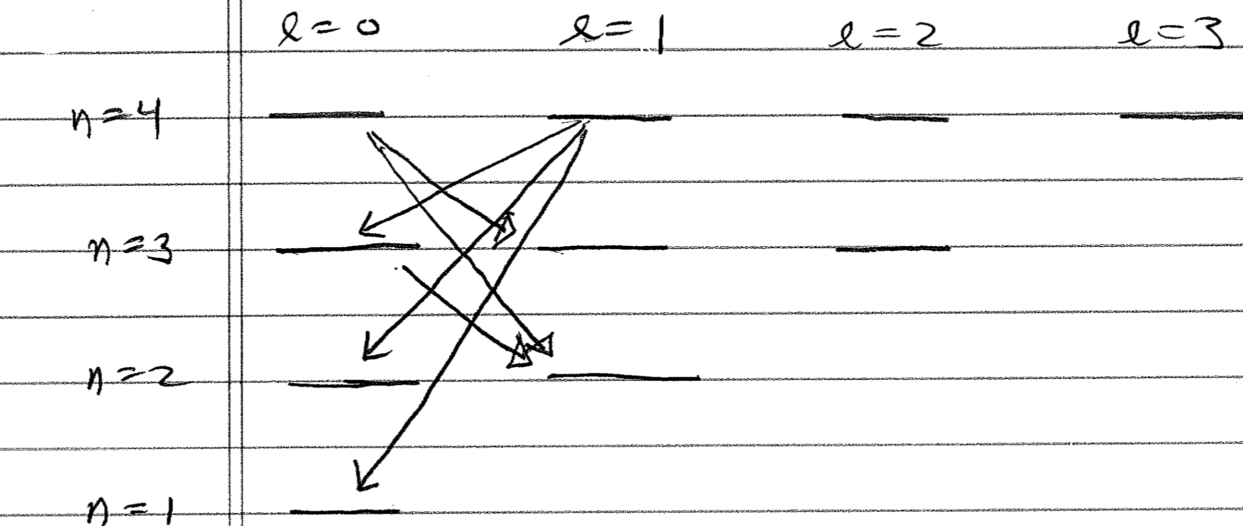
$$\Rightarrow \boxed{\Delta m = 0, \pm 1}$$

Q: How else to understand this?
what is spin of photon?
A: spin 1 $m = 0, \pm 1$

Another comm reln $[L^2,[L^2,\vec{r}]] = 2\hbar^2(\vec{r}L^2 + L^2\vec{r})$

insert this inside $\langle n'\ell'm'|\quad|n\ell m\rangle$

$\Rightarrow$ $\Delta\ell = \pm 1$
algebra



2s ψ_{200} is "stuck"

metastable state long lifetime

We talked about a spatially uniform, but time dependent, electric field. If we are really interested in light incident on an atom

$$\hat{H} = \frac{1}{2m}\left(\vec{p} - \frac{e}{c}\vec{A}(r,t)\right)^2 + V(r)$$

perturbation is

$$-\frac{e}{2mc}\left(\vec{p}\cdot\vec{A} + \vec{A}\cdot\vec{p}\right)$$

Need matrix elements of $\vec{p}$ in, eg Hydrogenic states

Q: Any ideas about this

$$\hat{p} = \frac{im}{\hbar}\left[\hat{H}_0, \hat{r}\right]$$

so $$\langle n'|\hat{p}|n\rangle = \frac{-im}{\hbar}(E_{n_0} - E_{n'_0})\langle n'|\hat{r}|n\rangle$$

our selection rule discussion for $\hat{r}$ carries over to $\hat{p}$

$$\vec{A}(r\,t) = \hat{\epsilon} A_0 \cos(\vec{k}\cdot\vec{r} - \omega t)$$

Q: what is this — A: Polarization

Q: any reln to $\vec{k}$ — A: $\hat{\epsilon}\cdot\vec{k} = 0$

$$\vec{A} = \frac{A_0}{2}\hat{\epsilon}\left[e^{i(\vec{k}\cdot\vec{r}-\omega t)} + e^{-i(\vec{k}\cdot\vec{r}-\omega t)}\right]$$

$\vec{p}\cdot\vec{A}$ involves actually $\vec{p}\cdot\hat{\epsilon}\, e^{i(\vec{k}\cdot\vec{r})}$

Electric dipole approximation $e^{i(\vec{k}\cdot\vec{r})} = \underline{1}$

HW 5-2

Q: why true / plausible

A: For visible light $\lambda \sim 600$ nm

Bohr radius $a_0 \sim .05$ nm

$.5\,\mathring{A} = .5\cdot 10^{-8}$ cm

$= .5\cdot 10^{-10}$ m