5.4 Variational Method

Estimating ground state when exact soln not avail.

Pick trial ket $|\tilde{0}\rangle$ s.t. $\bar{H} = \dfrac{\langle\tilde{0}|H|\tilde{0}\rangle}{\langle\tilde{0}|\tilde{0}\rangle}$.

Thm We claim that the upper bound of ground state E_0 is

$$E_0 \leq \bar{H}.$$

Pf. Let $|k\rangle$ true eng. ket s.t. $H|k\rangle = E_k|k\rangle$

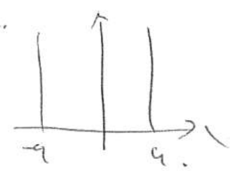
then $|\tilde{0}\rangle = \sum_{k=0}^{\infty} |k\rangle\langle k|\tilde{0}\rangle$

$$\bar{H} = \frac{\sum_k |\langle k|\tilde{0}\rangle|^2 E_k}{\langle\tilde{0}|\tilde{0}\rangle} = \frac{\sum_k |\langle k|\tilde{0}\rangle|^2 (E_k - E_0)}{\langle\tilde{0}|\tilde{0}\rangle} + E_0 \geq E_0 \quad //$$

Error of estimate?

If order one: $\langle k|\tilde{0}\rangle \sim O(\varepsilon)$ when $k \neq 0$ then $\bar{H} - E_0 \sim O(\varepsilon^2)$

ex.



exact soln: $\langle x|0\rangle = \frac{1}{\sqrt{a}} \cos\left(\frac{\pi x}{2a}\right)$

$$E_0 = \frac{\hbar^2}{2m}\frac{\pi^2}{4a^2}$$

Assume unknown.

Since wavefun. vanished at $\pm a$ and no wiggles, we let $\langle x|\tilde{0}\rangle = a^2 - x^2$.

then by definition, $\bar{H} = \dfrac{\int_{-a}^{a}(a^2-x^2)\left(\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\right)(a^2-x^2)\,dx}{\int_{-a}^{a}(a^2-x^2)^2 dx} = \dfrac{10}{\pi^2}\dfrac{\pi^2\hbar^2}{8a^2m} \approx 1.0132\, E_0$!

ex A sophisticated approach

Let $\langle x|\tilde{0}\rangle = |a|^\lambda - |x|^\lambda$ work out this integral

$$\bar{H} = \frac{\int_{-a}^{a}(|a|^\lambda - |x|^\lambda)\left(\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\right)(|a|^\lambda - |x|^\lambda)\,dx}{\int_{-a}^{a}(|a|^\lambda - |x|^\lambda)^2 dx} = \left[\frac{(\lambda+1)(2\lambda+1)}{(2\lambda-1)}\right]\frac{\hbar^2}{4ma^2}$$

$\dfrac{\partial \bar{H}}{\partial\lambda} = 0 \Rightarrow \lambda = \dfrac{1+\sqrt{6}}{2} \approx 1.72$ and $\bar{H}_{min} = \left(\dfrac{5+2\sqrt{6}}{\pi^2}\right)E_0 \approx 1.00298\, E_0$!

ex hydrogen atom, let $\langle x|\tilde{0}\rangle \sim e^{-r/a}$

$$H = \frac{p^2}{2m} - \frac{e^2}{r} = \frac{-\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{e^2}{r}$$

$$\bar{H} = \frac{\int_0^\infty e^{-r/a} H e^{-r/a} r^2 dr}{\int_0^\infty r^2 e^{-2r/a} dr} = \frac{\frac{a(\hbar^2 - 2ae^2m)}{8m}}{\frac{a^3}{4}} = \frac{\hbar^2 - 2ae^2m}{2a^2m}$$

~~a as variational param~~

Set $\dfrac{\partial\bar{H}}{\partial a} = 0 \Rightarrow a = \dfrac{\hbar^2}{me^2} = a_0$ thus $\bar{H} = -\dfrac{me^4}{2\hbar^2} = -\dfrac{e^2}{a_0}$ Correct E_0 !

Time-dependent Potentials

Consider $H = H_0 + V(t)$ where $H_0|n\rangle = E_n|n\rangle$

At $t=0$ $|\alpha\rangle = \sum_n C_n(0)|n\rangle$

Quest for, $C_n(t)$ for $t>0$ s.t

$$\boxed{|\alpha, t_0=0; t\rangle_S = \sum_n C_n(t) e^{-\frac{iE_nt}{\hbar}}|n\rangle}$$

two types of time depend.

$e^{-\frac{iE_nt}{\hbar}}$ due to H and

$C_n(t)$ due to $V(t)$ and prob. of finding $|n\rangle$ is $|C_n(t)|^2$

Introduce Interaction Picture "I"

<u>Def</u> $\boxed{|\alpha, t_0; t\rangle_I = e^{\frac{iH_0t}{\hbar}}|\alpha, t_0; t\rangle_S}$ s.t $|\alpha, t_0\rangle_I = |\alpha, t_0\rangle_S$

Observable in IP

$$\boxed{A_I \equiv e^{\frac{iH_0t}{\hbar}} A_S e^{-\frac{iH_0t}{\hbar}}}$$

Recall in H.P

$$|\alpha\rangle_H = e^{\frac{iHt}{\hbar}}|\alpha, t_0; t\rangle_S$$

$$A_H = e^{\frac{iHt}{\hbar}} A_S e^{-\frac{iHt}{\hbar}}$$

Consider S.E

$$i\hbar\frac{\partial}{\partial t}|\alpha, t_0; t\rangle_I = \left[-H_0 e^{\frac{iHt}{\hbar}} + e^{\frac{iH_0t}{\hbar}}(H_0 + V(t))\right]|\alpha, t_0; t\rangle_S = e^{\frac{iH_0t}{\hbar}} V(t) e^{-\frac{iH_0t}{\hbar}}|\alpha, t_0; t\rangle_I$$

so $$\boxed{i\hbar\frac{\partial}{\partial t}|\alpha, t_0; t\rangle_I = V_I|\alpha, t_0; t\rangle_I}$$

<u>Remark</u>: SE like where $|\alpha, t_0; t\rangle_I$ evolution determined by V_I

Consider HEOM

$$\boxed{\frac{dA_I}{dt} = \frac{1}{i\hbar}[A_I, H_0]}$$

<u>Remark</u>: Again Heisenberg like w/ evolution due to H_0

Between S.P & I.P,

$$\boxed{|\alpha, t_0; t\rangle_I = \sum_n C_n(t)|n\rangle}$$ thus $\langle n|\alpha, t_0; t\rangle_I = C_n(t)$

From eed.

$i\hbar\frac{\partial}{\partial t}|\alpha, t_0; t\rangle_I = V_I|\alpha, t_0; t\rangle_I$, we'll have

$$i\hbar\frac{\partial}{\partial t}C_n(t) = e^{i\omega_{nm}t}V_{nm}C_m(t) \quad \text{w/ } \omega_{nm} = \frac{E_n - E_m}{\hbar} = -\omega_{mn}$$

Couple diff. eqn

$$\Rightarrow i\hbar\begin{pmatrix}\dot{C}_1\\ \dot{C}_2\\ \vdots\end{pmatrix} = \begin{pmatrix}V_{11} & V_{12}e^{i\omega_{12}t} & \cdots\\ V_{21}e^{i\omega_{21}t} & V_{22} & \\ \vdots & & \ddots\end{pmatrix}\begin{pmatrix}C_1\\ C_2\\ \vdots\end{pmatrix}$$

ex two-state problems.

Can be solved analytically if ground state populate at $t=0$ i.e $C_1(0)=1$ $C_2(0)=0$

$H_0 = E_1|1\rangle\langle 1| + E_2|2\rangle\langle 2|$

let $V(t) = \gamma e^{i\omega t}|1\rangle\langle 2| + \gamma e^{-i\omega t}|2\rangle\langle 1|$ off diag. so $V_{11}=V_{22}=0$

$V_{12} = \gamma e^{i\omega t}$ $V_{21} = \gamma e^{-i\omega t}$

couple diff

$$i\hbar \begin{pmatrix} \dot{C}_1 \\ \dot{C}_2 \end{pmatrix} = \begin{pmatrix} 0 & \gamma e^{i\omega t - i\omega_{21} t} \\ \gamma e^{-(i\omega t + i\omega_{21})t} & \gamma \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix}$$

thus, $i\hbar \dot{C}_1 = \gamma e^{i\bar{\omega} t} C_2$ w/ $\bar{\omega} \equiv (\omega - \omega_{21})$

(*) $i\hbar \dot{C}_2 = \gamma e^{-i\bar{\omega} t} C_1$

Ansatz, $C_1 = a_1(t) e^{\frac{i\bar{\omega} t}{2}}$, $C_2 = a_2(t) e^{-\frac{i\bar{\omega} t}{2}}$ $\Rightarrow$ $i\hbar \dot{a}_1 - \frac{\hbar\bar{\omega}}{2} a_1 = \gamma a_2 e^{-\frac{i\bar{\omega}}{2}t}$, $i\hbar \dot{a}_2 + \frac{\hbar\bar{\omega}}{2} a_2 = \gamma a_1 e^{\frac{i\bar{\omega}}{2}t}$

Ansatz $a_1 = a_{10} e^{+i\Omega t}$, $a_2 = a_{20} e^{+i\Omega t}$ $\Rightarrow$ $(\hbar\Omega - \frac{\hbar\bar{\omega}}{2}) a_{20} = -\gamma a_{10} e^{\frac{i\bar{\omega}t}{2}}$, $(\hbar\Omega + \frac{\hbar\bar{\omega}}{2}) a_{10} = -\gamma a_{20} e^{-\frac{i\bar{\omega}t}{2}}$

thus $\Omega = \pm \left(\frac{\gamma^2}{\hbar^2} + \frac{\bar{\omega}^2}{4} \right)^{1/2}$

Now consider $a_1(t) = \alpha e^{i\Omega t} + \beta e^{-i\Omega t}$, $a_2(t) = r_\alpha \alpha e^{i\Omega t} + r_\beta \beta e^{-i\Omega t}$ s.t $\alpha + \beta = 1$, $r_\alpha \alpha + r_\beta \beta = 0 \Rightarrow \alpha(1 - \frac{r_\alpha}{r_\beta}) = 1$

then $a_2(t) = 2i r_\alpha \alpha \sin\Omega t$

Recalled $C_2(t) = a_2(t) e^{-\frac{i(\omega - \omega_{21})}{2}t} = 2i r_\alpha \alpha \sin\Omega t \, e^{-\frac{i(\omega-\omega_{21})}{2}t}$

then $\dot{C}_2(0) = 2i r_\alpha \alpha \Omega$ (apply I.C)

From (*) $i\hbar \dot{C}_2(0) = \gamma C_1(0) \Rightarrow i\hbar(2i r_\alpha \alpha)\Omega = \gamma$ thus $2i r_\alpha \alpha = \frac{\gamma}{i\hbar\Omega}$

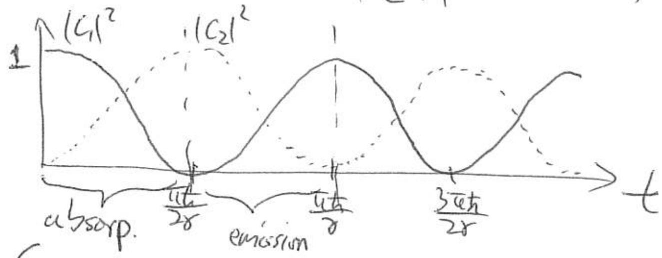
$$C_2(t) = \frac{\gamma}{i\hbar\Omega} \sin\Omega t \, e^{-\frac{i(\omega-\omega_{21})t}{2}}$$

$$|C_2(t)|^2 = \frac{\gamma^2/\hbar^2}{\gamma^2/\hbar^2 + \frac{(\omega-\omega_{21})^2}{4}} \sin^2\left(\left[\frac{\gamma^2}{\hbar^2} + \frac{(\omega-\omega_{21})^2}{4} \right]^{1/2} t \right)$$

prob of finding upper state E_2. oscill. in freq Ω & resonance where $\omega = \omega_{21}$ $\Omega = \frac{\gamma}{\hbar}$!

ex two-state cont'

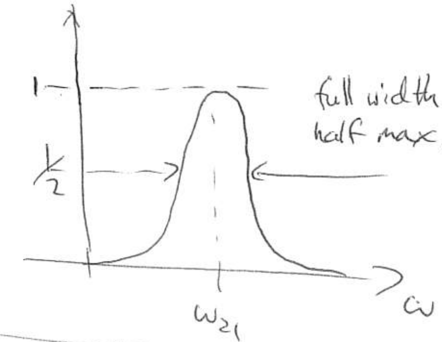
under resonance $|C_2(t)|^2 = \sin^2(\Omega t)$ $\quad |C_1(t)|^2 = \cos^2(\Omega t)$



from $V(t)$ to $|E_2\rangle$ $\qquad$ release to $V(t)$ back to $|E_1\rangle$

$$|C_{2,max}|^2 = \frac{\gamma^2/\hbar^2}{\gamma^2/\hbar^2 + \frac{(\omega-\omega_{21})^2}{4}}$$

Graphing $|C_{2,max}|^2$



full width def. by half max. $= \frac{4\gamma}{\hbar}$

Time-dependent Pertrb. theory

Recall $|\alpha, t_0; t\rangle_S = U(t, t_0)|\alpha, t_0\rangle_S$

let $\boxed{|\alpha, t_0; t\rangle_I = U_I(t, t_0)|\alpha, t_0; t_0\rangle_I \quad \text{where } U_I(t_0, t_0) = 1}$ — by construction

Consider $i\hbar\partial_t|\alpha, t_0; t\rangle_I = V_I|\alpha, t_0; t\rangle_I$

then we have

$$\boxed{i\hbar\partial_t U_I(t, t_0) = V_I U_I(t, t_0)}$$

integrate

$$\boxed{U_I(t, t_0) = 1 - \frac{i}{\hbar}\int_{t_0}^{t} dt' V_I(t') U_I(t', t_0)}$$

But U_I? Using recursion,

$$U_I(t, t_0) = 1 - \frac{i}{\hbar}\int_{t_0}^{t} dt' V_I(t') + \left(\frac{-i}{\hbar}\right)^2 \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' V_I(t') V_I(t'') \cdots$$

This is the Dyson Series.

Transition Probability

Given initial state $|i\rangle$

then $|i;t_0;t\rangle_I = U_I(t,0)|i\rangle = \sum_n |n\rangle\langle n|U_I(t,0)|i\rangle$

thus $C_n(t) = \langle n|U_I(t,0)|i\rangle$

Quest for connection between $U_I(t,t_0)$ & $U_s(t,t_0)$ — $U_s(t,t_0) = U(t,t_0)$

Recalled $|\alpha,t_0;t\rangle_I = e^{\frac{iH_0t}{\hbar}}|\alpha,t_0;t\rangle_s = e^{\frac{iH_0t}{\hbar}}U_s(t,t_0)|\alpha,t_0\rangle_s = e^{\frac{iH_0t}{\hbar}}U_s e^{-\frac{iH_0t}{\hbar}}|\alpha,t_0\rangle_I$

Thus $\boxed{U_I = e^{\frac{iH_0t}{\hbar}}U_s e^{-\frac{iH_0t}{\hbar}}}$

and $C_n(t) = e^{\frac{i(E_n-E_i)t}{\hbar}}\underbrace{\langle n|U_s(t,t_0)|i\rangle}_{\text{transition amplitude}}$ & $\boxed{|C_n(t)|^2 = |\langle n|U_s(t,t_0)|i\rangle|^2}$

Relation between Pertb theory & transition Prob. $|C_n(t)|^2$

Consider $t=t_0$ at state $|i\rangle$

then $|i,t_0;t_0\rangle_s = e^{-\frac{iE_it}{\hbar}}|i\rangle$

& $|i,t_0;t_0\rangle_I = e^{\frac{iH_0t_0}{\hbar}}|i,t_0;t_0\rangle_s = |i\rangle$

Now $t>0$,

$$|i,t_0;t\rangle_I = U_I(t,t_0)|i\rangle = \sum_n |n\rangle\langle n|U_I|i\rangle$$

so $\boxed{C_n(t) = \langle n|U_I(t,t_0)|i\rangle}$

Recall

$$U_I(t,t_0) = 1 - \frac{i}{\hbar}\int_{t_0}^{t}dt' V_I(t') + \left(\frac{-i}{\hbar}\right)^2\int_{t_0}^{t}dt'\int_{t_0}^{t'}dt'' V_I(t')V_I(t'')\cdots + \cdots$$

s.t

$$C_n(t) = \langle n|i\rangle - \frac{i}{\hbar}\int_{t_0}^{t}dt' e^{i\omega_{ni}t'}V_{ni}(t') + \cdots$$

Thus,

$$\boxed{\begin{aligned} C_n^{(0)}(t) &= \langle n|i\rangle = \delta_{ni} \\ C_n^{(1)}(t) &= -\frac{i}{\hbar}\int_{t_0}^{t}dt' e^{i\omega_{ni}t'}V_{ni}(t') \end{aligned}}$$

more common

$$C_n^{(2)}(t) = \left(\frac{-i}{\hbar}\right)^2\sum_m\int_{t_0}^{t}dt'\int_{t_0}^{t'}dt'' e^{i\omega_{nm}t'}V_{nm}(t')e^{i\omega_{mi}t''}V_{mi}(t'')$$

Thus transition probability for $|i\rangle \to |n\rangle$ is:

$$P(i\to n) = |C_n^{(1)}(t) + C_n^{(2)}(t) + \cdots|^2$$

ex Const. Pertrb

$$V(t) = \begin{cases} 0 & t<0 \\ V & t \geq 0 \end{cases} \quad V \text{ not } t \text{ depend.}$$

at $t=0$ we have $|i\rangle$ so $C_n^{(0)} = \delta_{ni}$; $C_n^{(1)} = \frac{-i}{\hbar}\int_{t_0}^{t} e^{i\omega_{ni}t'} V_{ni}(t')dt'$; $\omega_{ni} = \frac{E_n - E_i}{\hbar}$

here $V_{ni} = \langle n|V|i\rangle$.

$$C_n^{(1)} = -\frac{i}{\hbar}V_{ni}\int_0^t e^{i\omega_{ni}t'}dt' = \frac{V_{ni}}{E_n - E_i}(1 - e^{i\omega_{ni}t})$$

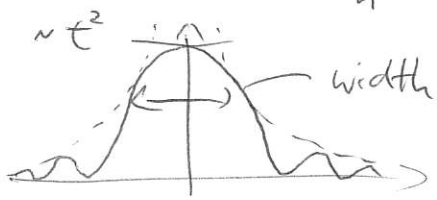
$$|C_n^{(1)}|^2 = \frac{|V_{ni}|^2}{|E_n - E_i|^2}(2 - 2\cos\omega_{ni}t) = \frac{4|V_{ni}|^2}{|E_n - E_i|^2}\sin^2\frac{(E_n - E_i)t}{2\hbar}$$

Remark: $|C_n^{(1)}|^2$ depends on $|V_{ni}|^2$ & $E_n - E_i$

Recast

$$|C_n^{(1)}|^2 = \frac{4|V_{ni}|^2}{\hbar}\frac{\sin^2\left(\frac{\omega_{ni}t}{2}\right)}{\omega_{ni}^2} \quad \text{and plot } |C_n^{(1)}|^2 \text{ v.s } \omega_{ni}$$

$\sim t^2$



width $\Rightarrow$ $\frac{\omega_{ni}t}{2} = \frac{\pi}{4}$ s.t $\sin^2(\ldots) \Rightarrow \frac{1}{2}$

width $= 2\omega_{ni} = \frac{\pi}{t}$ //

Remark: • states presents for short time has no definite energy.

• definite energy requires state to exist in many cycles.

• Peak at $\omega_{ni} \to 0$ thus has height of t^2

• In practice there are many states $E \sim E_n$ thus can be seen as continuum. and $\omega = \frac{E_n - E_i}{\hbar}$

• as t larges, then $|C_n^{(1)}|^2$ is ~~seen as~~ appreciable when

$$\boxed{t \sim \frac{2\pi}{|\omega|} = \frac{2\pi\hbar}{|E_n - E_i|}}$$

• from which we have

$$\boxed{\Delta t \, \Delta E \sim \hbar}$$

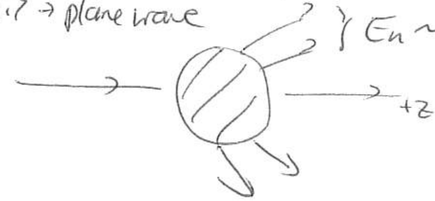
• Thus Δt small $\to$ broader peak.

• Δt small ΔE large energy thus not well measured.

• In reality, there're group of final states w/ $E_n \sim E_i$ (initial state)

So

$|i\rangle \to$ plane wave



$\} E_n \sim E_i$

• interested in total prob.

i.e. tran.prob sum over $E_n \simeq E_i$ $\boxed{\text{thus } \sum_{n, E_n \simeq E_i} |C_n^{(1)}|^2}$

Goal: $\sum_{n, E_n \approx E_i} |C_n^{(1)}(t)|^2$

Consider dos $\rho(E)dE$ within $(E, E+dE)$

then $\boxed{\sum_{n, E_n \approx E_i} |C_n^{(1)}(t)|^2 \cong \int dE_n \rho(E_n) |C_n^{(1)}|^2} = 4 \int dE_n \rho(E_n) \frac{|V_{ni}|^2}{|E_n - E_i|^2} \sin^2 \frac{(E_n - E_i)t}{2\hbar}$

<u>Analysis</u>. $t \to \infty$, $\lim_{t\to\infty} \frac{\sin^2\left(\frac{(E_n-E_i)t}{2\hbar}\right)}{(E_n - E_i)^2} = \frac{\pi t}{2\hbar} \delta(E_n - E_i)$

$\boxed{\text{note} \quad \lim_{\alpha\to\infty} \frac{\sin^2 \alpha x}{\alpha x^2} = \pi\delta(x)}$

then $\int dE_n \rho(E_n) |C_n^{(1)}|^2 = 4 \int dE_n \rho(E_n) |V_{ni}|^2 \frac{\pi t}{2\hbar} \delta(E_n - E_i) = \frac{2\pi}{\hbar} \overline{|V_{ni}|^2} \rho(E_n) t \Big|_{E_n \approx E_i}$

thus total trans. prob $\propto t$ for $t \gg 1$.

and $\boxed{\underline{\text{transition rate}} \quad \frac{d}{dt}\left(\sum_n |C_n^{(1)}|^2\right)} = \frac{2\pi}{\hbar} \overline{|V_{ni}|^2} \rho(E_n)_{E_n \approx E_i}$ Fermi's Golden rule!

write $\boxed{\underset{\substack{\text{group of}\\ \text{final states}}}{\omega_{i\to[n]}} = \frac{2\pi}{\hbar} \overline{|V_{ni}|^2} \rho(E_n)_{E_n \approx E_i}}$ or $\boxed{\omega_{i\to n} = \frac{2\pi}{\hbar} |V_{ni}|^2 \delta(E_n - E_i)}$ integrated over $\int dE_n \rho(E_n)$

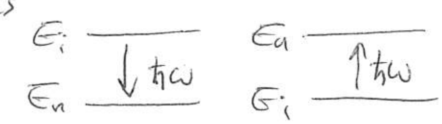
<u>ex</u> Harmonic Pertrb

$V(t) = Ve^{i\omega t} + V^\dagger e^{-i\omega t}$

then $C_n^{(1)} = -\frac{i}{\hbar} \int_0^t (V_{ni} e^{i\omega t'} + V_{ni}^\dagger e^{-i\omega t'}) e^{i\omega_{ni} t'} dt' = \frac{1}{\hbar}\left[\frac{1 - e^{i(\omega + \omega_{ni})t}}{\omega + \omega_{ni}} V_{ni} + \frac{1 - e^{-i(\omega - \omega_{ni})t}}{-\omega + \omega_{ni}} V_{ni}^\dagger\right]$

$t \to \infty$ $|C_n^{(1)}|^2$ appreciable if $\omega_{ni} + \omega \approx 0$ or $E_n \approx E_i - \hbar\omega$
$\omega_{ni} - \omega \approx 0$ or $E_n \approx E_i + \hbar\omega$

then $\omega_{i\to[n]} = \frac{2\pi}{\hbar} \overline{|V_{ni}|^2} \rho(E_n)_{E_n \approx E_i - \hbar\omega}$
$\omega_{i\to[n]} = \frac{2\pi}{\hbar} \overline{|V_{ni}^\dagger|^2} \rho(E_n)_{E_n \approx E_i + \hbar\omega}$ thus



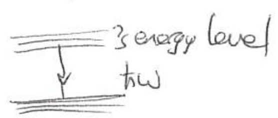
note $\langle i|V^\dagger|n\rangle = \langle n|V|i\rangle^* \Rightarrow |V_{ni}|^2 = |V_{in}^\dagger|^2$

thus. $\frac{\text{emission rate}}{\text{density of final state}} = \frac{\text{absorption rate}}{\text{"}}$

<u>Summarize</u>

constant pertrb. tran. prob appreciable for $|i\rangle \to |n\rangle$ if $E_n \approx E_i$
harmonic pertrb. " " " for $|i\rangle \to |n\rangle$ if $E_n \approx E_i \mp \hbar\omega$

ex



5.8 Application

Interaction w/ classic radiation field.

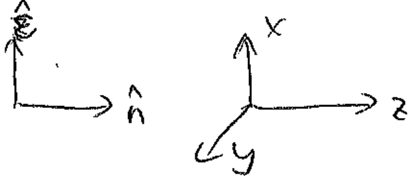
- electron w/ classic radiation

$$H = \frac{\vec{p}^2}{2m} + e\phi(\vec{x}) - \frac{e}{m_e c}\vec{A}\cdot\vec{p} \qquad b/c\ \nabla\cdot\vec{A}=0 \quad \text{and } \vec{A}^2 \text{ omitted.}$$

For monochromatic field of plane wave

$$\vec{A} = 2A_0\hat{\varepsilon}\cos\left(\frac{\omega}{c}\hat{n}\cdot\vec{x} - \omega t\right)$$

polarized direct. propagate direct.



recast.

$$\vec{A} = A_0\hat{\varepsilon}\left[e^{\frac{i\omega}{c}\hat{n}\cdot\vec{x} - i\omega t} + e^{-i\frac{\omega}{c}\hat{n}\cdot\vec{x} + i\omega t}\right]$$

$$\frac{-e}{m_e c}\vec{A}\cdot\vec{p} = -\frac{eA_0}{m_e c}\hat{\varepsilon}\cdot\vec{p}\,[\ \sim\ ] \qquad \text{as} \quad V(t) = Ve^{i\omega t} + V^{+}e^{-i\omega t}$$

So $V^{+} = \frac{eA_0}{m_e c}\left(e^{\frac{i\omega}{c}\hat{n}\cdot\vec{x}}\hat{\varepsilon}\cdot\vec{p}\right)$ absorption.

thus, $$\omega_{i\to n} = \frac{2\pi}{\hbar}\frac{e^2}{m_e^2 c^2}|A_0|^2\left|\langle n|e^{\frac{i\omega}{c}\hat{n}\cdot\vec{x}}\hat{\varepsilon}\cdot\vec{p}|i\rangle\right|^2\delta(E_n - E_i - \hbar\omega)$$

Remark

- if $|n\rangle$ cont' then $\omega_{i\to n}$ integrate over $\rho(E_n)dE_n$
- if $|n\rangle$ discrete then

$$\delta(\omega - \omega_{ni}) = \lim_{\gamma\to 0}\left(\frac{\gamma}{2\pi}\right)\frac{1}{[(\omega-\omega_{ni})^2 + \frac{\gamma^2}{4}]}$$

note $\lim_{a\to\infty}\frac{\sin^2 ax}{x^2} = a\pi\delta(x)$

- Incident EM wave not perfectly monochromatic thus has finite freq. width.

Absorption cross section

$$\sigma_{abs} = \frac{\text{(Energy / unit time) absorbed by atom}(i\to n)}{\text{energy flux of rad. field}}$$

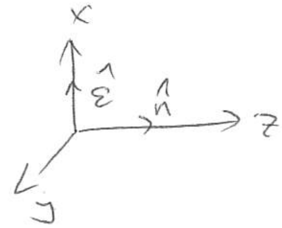
note $U = \frac{1}{2}\left(\frac{E_{max}^2}{8\pi} + \frac{B_{max}^2}{8\pi}\right)$ note $\vec{E} = -\frac{1}{c}\frac{\partial\vec{A}}{\partial t}$ $\vec{B} = \nabla\times\vec{A}$

Energy flux $cU = \frac{1}{2\pi}\frac{\omega^2}{c}|A_0|^2$

thus $$\sigma_{abs} = \frac{\hbar\omega\times\omega_{i\to n}}{cU} = \frac{4\pi^2\hbar}{m_e^2\omega}\underbrace{\left(\frac{e^2}{\hbar c}\right)}_{\alpha\sim\frac{1}{137}}\left|\langle n|e^{\frac{i\omega}{c}\hat{n}\cdot\vec{x}}\hat{\varepsilon}\cdot\vec{p}|i\rangle\right|^2\delta(E_n - E_i - \hbar\omega)$$

• Electric Dipole Approx.

Evaluate $\langle n | e^{i\frac{\omega}{c}\hat{n}\cdot\vec{x}} \hat{\varepsilon}\cdot\hat{p} | i \rangle$



Conside $\frac{\omega}{c}\hat{n}\cdot\vec{x}$

- size of $|\vec{x}| \sim R_{atom}$ (order of atom)
- binding energy

$$\hbar\omega \sim \frac{Ze^2}{R_{atom}} \quad , \quad R_{atom} \sim \frac{Z}{\omega}\underbrace{\left(\frac{e^2}{\hbar c}\right)}_{\alpha} c = Z\frac{c}{\omega}\frac{1}{137}$$

for $\lambda = \frac{c}{\omega}$, $\frac{R_{atm}}{\lambda} \sim \frac{Z}{137} \ll 1$ for light atom (Z small)

thus $e^{i\frac{\omega}{c}\hat{n}\cdot\vec{x}} \simeq 1 + \underbrace{i\frac{\omega}{c}\hat{n}\cdot x}_{\ll 1}$

and $\langle n | e^{i\frac{\omega}{c}\hat{n}\cdot\vec{x}} \hat{\varepsilon}\cdot\hat{p} | i \rangle \simeq \hat{\varepsilon}\cdot\langle n | \vec{p} | i \rangle = \langle n | P_x | i \rangle$

Recalled $[x, H_0] = \frac{i\hbar P_x}{m}$

$$\langle n | P_x | i \rangle = \langle n | \frac{m}{i\hbar}[x, H_0] | i \rangle = \frac{m}{i\hbar}(E_n - E_i)\langle n | X | i \rangle$$

$$\langle n | P_x | i \rangle = i m \omega_{ni} \underbrace{\langle n | X | i \rangle}_{\text{elec. dipole. approx.}}$$

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here $\vec{x}$ is $T^{(1)}_q$ $k=1$ $q=\pm 1$ and $m' = m \pm 1$ $|j'-j| = 0,1$

if $\hat{\varepsilon} = \hat{z}$ $m' = m$

So

$$\sigma_{abs} = 4\pi^2\alpha\,\omega_{ni}\,|\langle n | X | i \rangle|^2\,\delta(\omega - \omega_{ni})$$

$$\int \sigma_{abs}(\omega)\,d\omega = \sum_n 4\pi^2\alpha\,\omega_{ni}\,|\langle n | x | i \rangle|^2$$

define $\boxed{f_{ni} = \frac{2m\omega_{ni}}{\hbar}|\langle n | x | i \rangle|^2 \quad \text{and} \quad \sum_n f_{ni} = 1}$ Thomas-Reiche-Kuhn Sum Rule

then $\sum_n (E_n - E_i)|\langle n | x | i \rangle|^2 = \frac{\hbar^2}{2m}$

Hamiltonian independent

Now $\int \sigma_{abs}(\omega)\,d\omega = \frac{4\pi^2\alpha\hbar}{2m_e} = \frac{2\pi^2 e^2}{m_e c}$