Lecture 5

Time-dependent perturbation theory

$$i\hbar\,\partial_t|\psi\rangle = H|\psi\rangle$$

$$H(t) = H^\circ + H'(t)$$

t-dependent perturbation
e.g. EM radiation, photons, (NMR) t-dependent $\vec{B}(t)$-field, etc. (stimulated emission)

many types: adiabatic, sudden, periodic.

Question:
If at $t=0$, system is in eigenstate $|i^\circ\rangle$ of H° what is amplitude for system to be in eigenstate $|f^\circ\rangle$?

In general: $|\psi(t)\rangle = \hat{U}_t|\psi(0)\rangle$

$$|\psi(t)\rangle = e^{-\frac{i}{\hbar}\int_0^t \hat{H}(t)}|\psi(0)\rangle$$

$$A_{\psi_0\to f} = \langle f^\circ|\psi(t)\rangle = \langle f^\circ|\hat{U}_t|\psi_0\rangle$$

0th order: $H = H^\circ \Rightarrow$

$$A_{i\to f} = \langle f^\circ|e^{-\frac{i}{\hbar}H_0 t}|i^\circ\rangle = e^{-\frac{i}{\hbar}E_i^\circ t}\delta_{if}$$

vanishes for $f^\circ \neq i^\circ$

1st order perturbation theory:

$$|\psi(t)\rangle = \sum_n c_n(t)|n^\circ\rangle$$

$$c_n(t) = ?$$

$$i\hbar\,\partial_t |\psi\rangle = \left(H_0 + H_1(t)\right)|\psi\rangle$$

$$i\hbar \sum_n \dot{c}_n(t)|n^\circ\rangle = \sum_n E_n^\circ c_n(t)|n^\circ\rangle + \sum_n H_1(t)\, c_n(t)|n^\circ\rangle$$

$\langle f^\circ|$ $$i\hbar\, \dot{c}_f(t) = E_f^\circ c_f(t) + \sum_n \langle f^\circ|H_1(t)|n^\circ\rangle c_n(t)$$

take: $c_f(t) = d_f(t)\, e^{-\frac{i}{\hbar}E_f^\circ t}$

$$\boxed{i\hbar\, \dot{d}_f = \sum_n \langle f^\circ|H_1(t)|n^\circ\rangle e^{i\omega_{fn}t} d_n(t)}$$

$$\left(\omega_{fn} = (E_f^\circ - E_n^\circ)/\hbar\right)$$

$|\psi(0)\rangle = |i^\circ\rangle \Rightarrow d_n(0) = \delta_{ni}$

P.T. in H_1:

0^{th} order: $\dot{d}_f = 0 \Rightarrow d_f = \delta_{fi}$

1^{st} order: $\dot{d}_f(t) = \frac{-i}{\hbar}\langle f^\circ|H'(t)|i^\circ\rangle e^{i\omega_{fi}t}$

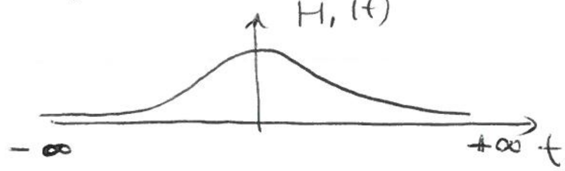
$$\Rightarrow d_f(t) = \delta_{fi} - \frac{i}{\hbar}\int_0^t \langle f^\circ|H'(t')|i^\circ\rangle e^{i\omega_{fi}t'}dt'$$

2^{nd} order: use above $d_f(t)$ inside S.Eqn on r.h.s. & full d_f on l.h.s.

$\vdots$ ok if $|d_f(t)| << 1$ (for $f \neq i$)

<u>Ex</u>: Harmonic oscillator in $|0\rangle$ at $t = -\infty$

$$H_1(t) = -e\mathcal{E}x\, e^{-t^2/\tau^2}$$



Prob in $|n\rangle = P_n(t=\infty) = ?$

$$d_n(\infty) = \frac{-i}{\hbar}\int_{-\infty}^{\infty}(-e\mathcal{E})\langle n|x|0\rangle e^{-t'^2/\tau^2} e^{in\omega t'}\, dt'$$

$$x = \frac{x_0}{\sqrt{2}}(a + a^+)$$

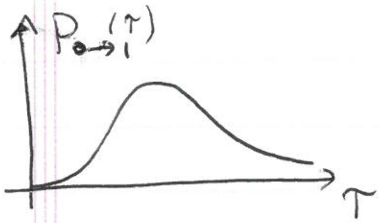
$$\Rightarrow d_n(\infty) = d_1(\infty)\,\delta_{n1}$$

$$= \delta_{n1}\,\frac{ie\mathcal{E}}{\hbar}\left(\frac{\hbar}{2m\omega}\right)^{1/2}\int_{-\infty}^{\infty} dt\, e^{-t^2/\tau^2} e^{i\omega t}$$

$$= \delta_{n1}\, ie\mathcal{E}\left(\frac{\pi\tau^2}{\hbar 2m\omega}\right)^{1/2} e^{-\omega^2\tau^2/4}$$

(dipole transition)

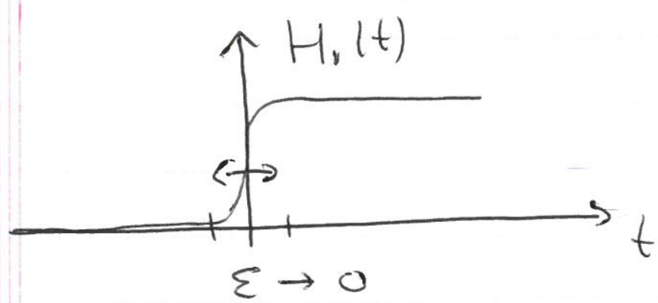
$$\Rightarrow \underline{P_{0\to n} = \delta_{n1}\,\frac{e^2\mathcal{E}^2\pi\tau^2}{2m\omega\hbar}\, e^{-\omega^2\tau^2/2}}$$



$\tau \to 0$ $\quad P_{0\to1} \to 0$, acts for <u>too short</u> time.

$\tau \to \infty$ $\quad P_{0\to1} \to 0$, acts <u>too slowly</u>, adiabatically, that systems stays in $|0\rangle$ state.

A. Sudden perturbation



integrate S. Eqn of $-\frac{\varepsilon}{2} < t < \frac{\varepsilon}{2}$

$$i\hbar \partial_t |\psi\rangle = H|\psi\rangle$$

$$\Rightarrow \quad |\psi(\varepsilon/2)\rangle - |\psi(-\varepsilon/2)\rangle = -\frac{i}{\hbar}\int_{-\varepsilon/2}^{\varepsilon/2} H|\psi\rangle dt$$

if finite

$$|\psi_{\text{after}}\rangle - |\psi_{\text{before}}\rangle \underset{\varepsilon \to 0}{=} 0$$

Already have seen this e.g. on final (shifted h.o.), also previous example with $\tau \to 0$.

Sudden means $\tau <<$ natural time scale for system's evolution, e.g. ω_0^{-1}

$\frac{\hbar}{\tau} >>$ gaps.

Ex. $\quad H = H_0 + \Theta(t) H_1$

$$|\psi(0)\rangle = |n^0\rangle \qquad (H_0|n^0\rangle = E_n^0|n^0\rangle$$

$$|\psi(t=0^+)\rangle = |n^0\rangle \;, \text{ but } \quad H = H_0 + H_1$$

$(H_0 + H_1)|n^0\rangle \neq E|n^0\rangle \Rightarrow |\psi(t)\rangle$ will evolve nontrivially with $U_t = e^{-\frac{i}{\hbar}\int_0^t H dt'}$

B. Adiabatic perturbation (also Landau - Zener)

$H(t)$ changes <u>very</u> <u>slowly</u>

Q: How slowly, compared to what?

A: rate of change $\gamma = \dfrac{\dot{H}}{H} \ll \omega_{nm}$

is smaller than smallest "natural" frequency in the problem, i.e. compared to <u>smallest</u> gap/$\hbar$.

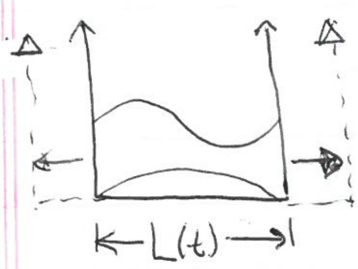
If so $\Rightarrow$ adiabatic theorem applies:

$$|n(0)\rangle \xrightarrow[T]{} |n(T)\rangle$$

where $H(0)|n(0)\rangle = E_n(0)|n(0)\rangle$ &

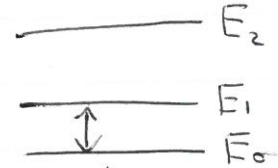
$$H(T)|n(T)\rangle = E_n(T)|n(T)\rangle$$

Ex.



$$\gamma = \frac{\dot{L}}{L} \ll \frac{\left(\frac{2\pi}{L}\hbar\right)^2}{2m\hbar} = \omega_{01}$$

$$\approx \underbrace{\frac{\hbar}{mL^2}}_{=\left(\frac{\hbar}{mL}\right)/L} = \frac{v}{L} \approx \frac{\hbar/Lm}{L}$$



Hence $H_1(t)$ that turns on and then shuts off (if slowly enough) leaves system in initial eigenstate, i.e., unchanged.

Connection of time-dependent <u>adiabatic p.t.</u> to time-independent p.t.

<u>ex</u>: $H(t) = H^\circ + e^{t/T} H'$, $\quad -\infty \le t \le 0$

In $T \to \infty$ limit (adiabatic), eigenstates of

$H(0) = H^\circ + H'$ can be obtained from t.d.p.t.

At $t = -\infty$ $\quad |n^\circ\rangle$ eigenstate of H°

$\Rightarrow$ $|n\rangle$ - eigenstate of $H(t=0) = H_0 + H_1$

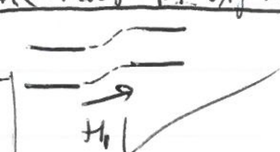
is to 1st order: $|n\rangle = \sum_m d_m(0) |m^\circ\rangle$

$$\langle m^\circ|n\rangle = d_m(0) = -\frac{i}{\hbar}\int_{-\infty}^{0} \langle m^\circ|H'|n^\circ\rangle e^{t/T} e^{i\omega_{mn}t}\, dt$$

$$= (-i/\hbar)\,\frac{\langle m^\circ|H'|n^\circ\rangle}{1/T + i\omega_{mn}}$$

$|n^\circ\rangle \xrightarrow[H_1\,\nearrow]{} |n\rangle = \sum_m \langle m^\circ|n\rangle |m^\circ\rangle$

<u>time-indep. p.t. expansion</u>



$$T \to \infty \Rightarrow \boxed{\langle m^\circ|n\rangle = \frac{\langle m^\circ|H'|n^\circ\rangle}{E_n^\circ - E_m^\circ}}$$

$\Rightarrow |n^\circ\rangle \to |n\rangle$ no excited $|m\rangle$ states

we see what large T (adiabatic) means $\frac{\hbar}{T} << |E_m - E_n|$

$\Rightarrow$ no adiabatic perturbation for system with degeneracy.

<u>Analogy with WKB</u>: $H(T)$ slow $\Rightarrow |n^\circ\rangle \to |n(T)\rangle$ eigenstate of $H(T)$

just like if $H(x)$ changes slowly in space $|k^\circ\rangle = e^{ik^\circ x} \to e^{i\int^x k(x)\,dx}$.

Berry's geometric phase

Appears in systems changing adiabatically through a slow variation of a parameter in H, e.g. $H[R(t)]$, where $R(t)$ is nuclear position & H is e's Hamiltonian

$$H(t)|\psi(t)\rangle = i\hbar\,\partial_t|\psi(t)\rangle$$

What is $|\psi(t)\rangle = ?$

try:

$$|\psi(t)\rangle = c(t)\underbrace{|n(t)\rangle\, e^{-\frac{i}{\hbar}\int_0^t dt' E_n(t')}}$$

"naive" soln, where $|n(t)\rangle$

$\underline{c(t) = ?}$

$H(t)|n(t)\rangle = E_n(t)|n(t)\rangle$ is instantaneous eigenstate.

$$H(t)|n(t)\rangle c(t) e^{-\frac{i}{\hbar}\int_0^t E_n(t')dt'} = \Big(E_n(t)|n(t)\rangle c(t) + i\hbar\,\partial_t c(t)|n(t)\rangle + i\hbar\,\partial_t|n(t)\rangle c(t)\Big) e^{-\frac{i}{\hbar}\int_0^t dt' E_n(t')}$$

$$\partial_t c(t) = -c(t)\langle n(t)|\partial_t|n(t)\rangle$$

$$\Rightarrow \quad c(t) = c(0)\, e^{i\gamma(t)}$$

$$\boxed{\gamma(t) = i\int_0^t \langle n(t')|\,\partial_{t'}|n(t')\rangle dt'} \quad \underline{\text{Berry's Phase}}$$

$\underline{\text{purely real \#}}$, i.e., indeed just phase.

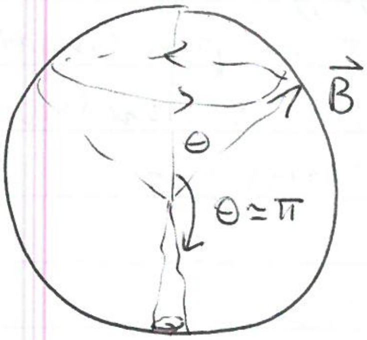
$$\gamma(t) = i\int \langle n(R(t))|\frac{\partial}{\partial R}|n(R(t'))\rangle\cdot\frac{d\vec{R}}{dt}\,dt' \equiv \frac{1}{\hbar}\oint \vec{A}_B\cdot d\vec{R}$$

Berry's vector potent.

Nontrivial consequences in systems with nonsimply connected space s.t. $\gamma = \oint \vec{A}_B\cdot d\vec{R} = \Phi_B$, when $\vec{\nabla}\times\vec{A}_B = \vec{B}_B \neq 0$

ex. spin ½ particle on a circle in azimuthal $\vec{B}$ field.

- Spin quantization through Berry's phase:



$$\gamma_\uparrow = 2\pi S(1-\cos\theta)$$

$$= \frac{S}{\hbar}\cdot \Omega$$

Ω ← solid angle subtended by $\vec{B}$

but to make sense

$$\gamma_\uparrow(\theta=\pi) = \gamma_\uparrow(0) = 2\pi n$$

$$2\pi S\cdot 2 = 2\pi n$$

$$\Rightarrow \boxed{S = \frac{\hbar}{2} n} \quad \checkmark \quad !!!$$

- Magnetic monopole $\vec{B}_g = \frac{g}{r^2}\hat{r} \Rightarrow \vec{\nabla}\cdot\vec{B}_g = 4\pi g\delta(\vec{r})$

$\vec{A}_g = ?$ s.t. $\vec{\nabla}\times\vec{A}_g = \vec{B}_g$

$$\vec{A} = -\frac{\hbar}{2}\hat{\varphi}\frac{(1-\cos\theta)}{R\sin\theta}$$ singular at $\theta=\pi$ (South pole)

$\Rightarrow$ Dirac string.

phase factor of electrically charged particle q moving in small loop around S. pole get

$$e^{i4\pi qg/\hbar c} = \underset{\text{require same as 0 flux}}{=} e^{i2\pi n}$$

$$= \frac{iq}{\hbar c}\oint \vec{A}\cdot d\vec{\ell}$$

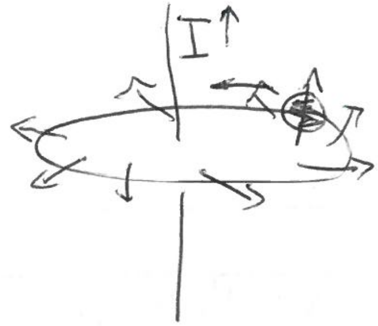
$$\Rightarrow \boxed{q = \left(\frac{\hbar c}{2g}\right) n \quad \text{quantization of charge!}}$$

$$\frac{q}{\hbar c}\oint \vec{A}\cdot d\vec{\ell} = \frac{q}{\hbar c}\oiint(\vec{\nabla}\times\vec{A})\cdot d\vec{S} = \frac{1}{\hbar c}\underbrace{\iiint \vec{\nabla}\cdot\vec{B}\,dv}_{4\pi gq}$$

$$= \frac{4\pi gq}{\hbar c} = 2\pi n. \quad \checkmark$$

Ex

5.8



$$\vec{B} = B_1 \hat{z} + B_2 \hat{\varphi}$$

naive: $$H = \frac{L^2}{2I} - c\,\vec{\sigma}\cdot\vec{B}(\phi) \qquad \phi = \varphi + \pi/2$$

$$H|m,\sigma_z\rangle = E_{m,\sigma_z}|m\,\sigma_z\rangle \qquad \nabla\cdot$$

take $$\langle \phi,\hat{n}|m\,\sigma_z\rangle = e^{im\phi}\begin{pmatrix}\cos\theta/2\\ i\sin\theta/2\, e^{i\phi}\end{pmatrix}$$

$$\Rightarrow E^{\text{naive}}_{m,\sigma_z} = \frac{\hbar^2 m^2}{2I} \mp cB, \qquad B = \sqrt{B_1^2+B_2^2}$$

with Berry's phase: $$H = \frac{(L_\varphi - A_B^{\sigma_z})^2}{2I} - c\,\vec{\sigma}\cdot\vec{B}(\phi)$$

$$\psi(\phi) = e^{im\phi}, \quad m\in\mathbb{Z} \text{ to ensure p.b.c.}$$

$$\Rightarrow E_{m,\uparrow} = \frac{(m\hbar - A_B^{\sigma_z})^2}{2I} \mp cB$$

$$A_B^{\uparrow} = i\hbar\langle\theta\phi|\frac{\partial}{\partial\phi}|\theta\phi\rangle = \underbrace{-\hbar\sin^2\frac{\theta}{2}}$$

$$\Rightarrow E_{m,\uparrow} = \frac{\hbar^2(m+\sin^2\frac{\theta}{2})^2}{2I} - BC$$

Monopole in φ (slow) d.o.f. $\quad \gamma = \frac{1}{\hbar}\oint \vec{A}_\varphi\cdot d\vec{l}$

$$H = -\vec{\sigma}\cdot\vec{B} = -\vec{\sigma}\cdot\vec{R} \Rightarrow B_{\text{Berry}} = \frac{\pm\hbar}{2}\frac{\hat{R}}{R^2} \qquad = -\int \sin^2\frac{\theta}{2}\,d\varphi$$

slowly varying $\qquad$ monopole $\qquad \gamma = -2\pi\,\frac{1}{2}(1-\cos\theta)$

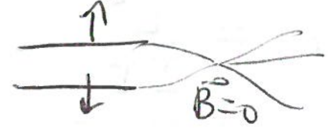
$$= -2\pi s(1-\cos\theta)$$

$s = 1/2$

$\cancel{\vec{\nabla}\cdot\vec{R} = 3}$

$\cancel{\int(\nabla\cdot R)\,d^3R = 3\cdot\frac{4}{3}\pi R^3 = 4\pi}$

$\vec{H} = -\vec{\sigma}\cdot\vec{B}$

monopole at "origin" in $\vec{B}$ space
at point of degeneracy of 

$$\vec{A}_B = i\hbar \langle n(B)|\vec{\nabla}_B|n(B)\rangle$$

$$\Rightarrow \vec{\mathcal{B}}_B = \mp \frac{\hbar}{2}\frac{\hat{B}}{2B^2}$$

monopole at origin of parameter space $\vec{B}$ defining $\vec{n}(B)$

Berry's phase consequences:

Ex: spin $\frac{1}{2}$ particle (neutral) moving in $\vec{r}$-depend. $\vec{B}$ field. $\Rightarrow$ orbital $\vec{\mathfrak{F}}$ field

$$|\psi_n(t)\rangle = e^{-\frac{i}{\hbar}\int_0^t dt' E_n(t')} |n(t)\rangle e^{i\gamma(t)}$$

$$= e^{-\frac{i}{\hbar}\int_0^t dt' E_n(R(t'))} |n(R(t))\rangle e^{\frac{i}{\hbar}\oint d\vec{R}\cdot\vec{A}^n_B(\vec{R})}$$

$$\vec{A}^n_B(\vec{R}) = i\hbar\langle n(R)|\vec{\nabla}_R|n(R)\rangle$$

gauge transf. $|n(R)\rangle \to e^{i\chi(R)}|n(R)\rangle$

$$A^n_B(R) \to A^n_B(R) - \hbar\frac{d\chi}{dR}$$

Effect of γ $(A_B(R))$ on dynamics of $\vec{R}(t)$:

- Path integral:

use

$$I = \int dR \sum_n |R, \hat{n}(R)\rangle \overbrace{\langle \hat{n}(R), R|}^{\langle R| \otimes \langle n(R)|}$$

adiabatic

$$\simeq \int dR\, |R, \hat{n}(R)\rangle\langle \hat{n}(R), R|$$

Born-Oppenheimer

$$\langle R(t)|U_t|R(0)\rangle = \prod_s \langle R(t_{s+1}), n(R(t_{s+1}))|\, e^{-\frac{i\varepsilon}{\hbar}H(\hat{R},\hat{P},\sigma)}\, |R(t_s), n(R(t_s))\rangle$$

B-O.: fix slow d.o.f.; solve fast $\Rightarrow E_n(R)$ corrects potential for slow d.o.f.

$$H_{slow}[\hat{R},\hat{P}] + H_{fast}[\hat{R},\sigma]$$

$$\left(H_{fast}[\hat{R},\sigma]\,|n(R)\rangle = E_n(R)\,|n(R)\rangle\right)$$

e.g. Born-Oppenheimer contrib. of e's to ionic potential

$$= \prod_s \langle R(t_{s+1})|\, e^{-\frac{i\varepsilon}{\hbar}H_{slow}[\hat{R},\hat{P}]}\, |R(t_s)\rangle\, e^{-\frac{i}{\hbar}E_n(R)} \underbrace{\langle n(R(t_{s+1}))|n(R(t_s))\rangle}_{\text{additional Berry's phase contribution.}}$$

Via Sch. Eqn

$$H|\psi\rangle = E|\psi\rangle$$

$$|\psi\rangle = \int dR\, \psi(R)\, |R, \hat{n}(R)\rangle$$

$$\langle R', \hat{n}(R')| H |\psi\rangle = \int dR\, \langle R'\, n(R')| H |R, n(R)\rangle \underbrace{\langle R\, n(R)|\psi\rangle}_{\psi(R)}$$

$$H = \frac{P^2}{2M} + V(R) + H_f(r, p, R)$$

$$H_f(r,p,R)|n(R)\rangle = E_n(R)|n(R)\rangle$$

$$\langle R'|\frac{P^2}{2M}|R\rangle = -\frac{\hbar^2}{2M}\delta''(R-R')$$

$$\Rightarrow H\psi(R) = -\frac{\hbar^2}{2M}\left[\langle n|\partial^2 n\rangle \psi(R) + 2\langle n|\partial_n\rangle \partial\psi + \partial^2\psi\right]$$

$$= \frac{1}{2M}\left(-i\hbar\partial_R - A_B\right)^2 + V_{eff}(R)$$

$$A_B = i\hbar\langle n|\partial_R n\rangle$$

$$V_{eff}(R) = V(R) + E_n(R) + V_B$$

$$V_B = \frac{\hbar^2}{2M}\left[\langle\partial n|\partial n\rangle - \langle\partial n|n\rangle\langle n|\partial n\rangle\right]$$

positive in the ground state

$$U_{R'R}(t) = \prod_s \sqrt{\frac{m}{2\pi\hbar i\varepsilon}}\; e^{\frac{i}{\hbar}\varepsilon\left[\frac{m}{2}\left(\frac{R(t_{s+1})-R(t_s)}{\varepsilon}\right)^2 - \bar{V}(R) - E_n(R)\right]}$$

$$\times \underbrace{\langle n(R(t_{s+1}))|n(R(t_s))\rangle}$$

$$\simeq 1 - \varepsilon \underbrace{\langle n(R)|\vec{\nabla}_R|n(R)\rangle}_{-\frac{i}{\hbar}A_B(t_s)} \cdot \underbrace{\frac{\vec{R}_{s+1}-\vec{R}_s}{\varepsilon}}_{V(t_s)}$$

$$\simeq e^{\frac{i}{\hbar}\varepsilon\, \vec{A}_B(t_s)\cdot\vec{V}(t_s)}$$

$$\Rightarrow U_{R'R}(t) = \int \mathcal{D}R(t)\; e^{\frac{i}{\hbar}S'[R(t)]}$$

$$S[R(t)] = \int_0^t \left[\frac{1}{2}m\dot{R}^2 - \underbrace{(\bar{V}(R)+E_n(R))}_{V_{eff}(R)} + \vec{A}_B(t')\cdot\dot{\vec{R}}(t')\right]dt'$$

Born-Oppenheimer

$$\Rightarrow H = \frac{(\vec{P}-\vec{A}_B)^2}{2m} + \bar{V}(R) + E_n(R)$$

orbital $\mathcal{B}$ field for neutral particle

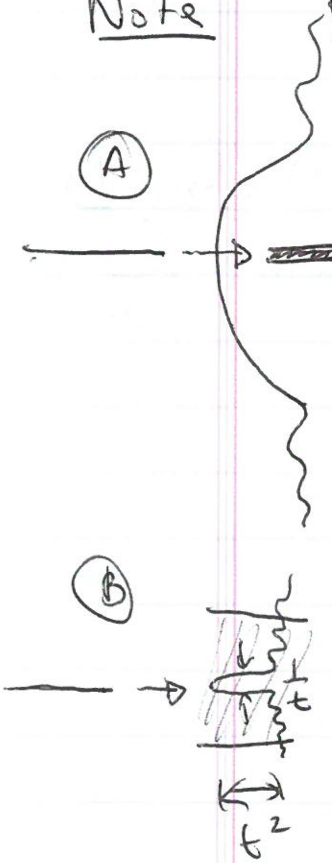
Note:

A more careful discretization, expanding $\langle n(R')|n(R)\rangle$ to $\mathcal{O}[(R'-R)^2]$ also produces a scalar potential

$$\Phi_n(R) = \frac{\hbar^2}{2m}\left[\langle\partial n|\partial n\rangle - \langle\partial n|n\rangle\langle n|\partial n\rangle\right]$$

(see Shankar, pg 598).

Subtleties about t^2 growth of $|c_n|^2(t)$



<u>Note</u> $$P_{i\to f} = \frac{|\langle f|H_1|i\rangle|^2}{\hbar^2}\left(\frac{\sin[(\omega_f-\omega_i-\omega)t/2]}{(\omega_f-\omega_i-\omega)/2}\right)^2$$

(A) $\simeq t^2$, for $\omega_f = \omega_i + \omega + \Delta$ with $\Delta \ll \frac{1}{t}$

e.g. represents prob. of trans. to a specific energy state (vanishing bandwidth) as in Rabi oscillations between 2 levels $|c_n|^2 \simeq \sin^2 \omega t$!

(B) $\simeq t$, for $\Delta \gg \frac{1}{t}$

transition into a band (of width Δ) of E_f levels. Integrate over Δ with $\Delta \gg$ width $\left(\frac{1}{t}\right)$ of $\left(\frac{\sin \Delta t}{\Delta}\right)^2$

$\Rightarrow$ latter "looks" like $\delta(\Delta)$

$$t^2 \searrow t = \underbrace{t^2}_{\text{height}} \cdot \underbrace{\frac{1}{t}}_{\text{width of accessible } E_f\text{'s.}}$$

Energy <u>non</u>conservation: $E_f - E_i - \hbar\omega \lesssim \frac{\hbar}{t}$

C. Periodic Perturbation

$$H'(t) = H' e^{-i\omega t}$$ (e.g. E&M field perturbing atom, causing transitions)

$$d_f(t) = \frac{-i}{\hbar}\int_0^t \langle f^\circ | H' | i^\circ \rangle e^{i(\omega_{fi}-\omega)t'} dt'$$

$$= -\frac{i}{\hbar}\langle f^\circ | H' | i^\circ \rangle \frac{e^{i(\omega_{fi}-\omega)t}-1}{i(\omega_{fi}-\omega)}$$

$$\Rightarrow P_{i\to f} = |d_f|^2 = \frac{1}{\hbar^2}|\langle f^\circ | H' | i^\circ\rangle|^2 \left\{\frac{\sin[(\omega_{fi}-\omega)t/2]}{(\omega_{fi}-\omega)t/2}\right\}^2 t^2$$

$\frac{\sin^2 x}{x^2}$ peaked at $x = 0$, width $\simeq \pi$, height 1

$$\Rightarrow |(\omega_{fi}-\omega)t| \le 2\pi \Rightarrow E_f^\circ - E_i^\circ = \hbar\omega \pm \frac{2\pi\hbar}{t}$$

$$\simeq \hbar\omega \text{ as } \omega t \to \infty$$

For $\omega t \to \infty$ $\left(\frac{\sin \Delta t}{\Delta}\right) \to 2\pi\delta(\Delta)$

After long time:

$$d_f(t) \underset{T\to\infty}{=} \frac{-i}{\hbar}\int_{-T/2}^{T/2} H'_{fi} e^{i(\omega_{fi}-\omega)t'} dt'$$

$$= -\frac{2\pi i}{\hbar} H'_{fi}\,\delta(\omega_{fi}-\omega)$$

Ex general

neutral particle, $S=\frac{1}{2}$ moving in an inhomogeneous $\vec{B}$ field

$$H = \frac{P^2}{2m} - \underbrace{\vec{\sigma}\cdot\vec{B}(R)}$$

note only Zeeman field.
no orbital effect from B
since neutral particle.

$$|\psi\rangle = |R\rangle \otimes |\hat{n}(R)\rangle$$

$$\begin{pmatrix} \cos\theta/2 \\ \sin\theta/2\, e^{i\varphi} \end{pmatrix}$$

$$\hat{n}(\theta,\varphi) = \frac{\vec{B}(R)}{|B|(R)}$$

$$\Rightarrow \boxed{H_{eff} = \frac{(\vec{P}-\vec{A}_B)^2}{2m} + V_{Berry}(R)}$$

$$|\hat{n}\rangle = |\hat{n}\uparrow\rangle = |GS\rangle$$

Berry's phase $\rightarrow$ orbital B field!

$$V_{Berry}(R) = \frac{\hbar^2}{2m}\left[\langle\partial n|(1 - \underbrace{|n\rangle\langle n|}_{\text{proj. onto excited states}})|\partial n\rangle\right]$$

$$V_B(R) = \frac{\hbar^2}{2m}\sum_e |\langle\partial n|n_e\rangle|^2 \qquad = \sum_e |n_e\rangle\langle n_e|$$

$$> 0 \quad \text{always repulsive}$$

$$\Rightarrow P_{i\to f} = \frac{4\pi^2}{\hbar^2} |H'_{fi}|^2 \underbrace{\delta(\omega_{fi}-\omega)\,\delta(\omega_{fi}-\omega)}_{\delta(\omega_{fi}-\omega)\,\underbrace{\frac{1}{2\pi}\int_{-T/2}^{T/2} e^{i0}\,dt'}_{T}}$$

$$\Rightarrow P_{i\to f} = \frac{2\pi}{\hbar} |\langle f|H'|i\rangle|^2 \delta(E_f - E_i - \hbar\omega)\, T$$

$$\Rightarrow \boxed{\text{Rate of transition} = \frac{P_{i\to f}}{T} = \frac{2\pi}{\hbar} |\langle f|H'|i\rangle|^2 \delta(E_f - E_i - \hbar\omega)}$$

Fermi's golden rule

energy conservation

Usually interested in Rate of transition into a range of state; e.g. width determined by detector resolution; or, interested in decay of a state $i \Rightarrow$ $\sum_f R_{i\to f}$, i.e sum over final states.

Note: since $|f\rangle$'s are distinct (not diff. paths to same state) $\Rightarrow$ sum prob. to get to $|f\rangle$'s.

$$\Rightarrow R_{i\to} = \sum_{\substack{\text{final}\\\text{state}\\f}} \frac{2\pi}{\hbar} |\langle f|H'|i\rangle|^2 \delta(E_f - E_i - \hbar\omega)$$

$$= \int dE_f\, \rho(E_f) \frac{2\pi}{\hbar} |\langle f|H'|i\rangle|^2 \delta(E_f - E_i - \hbar\omega)$$

Landau - Zener Transition

Landau Phys Z. Sowj **2**, 46 (1932)
Zener Proc. of R. Soc. **137**, 696 (1932)

Consider a 2-level system w/

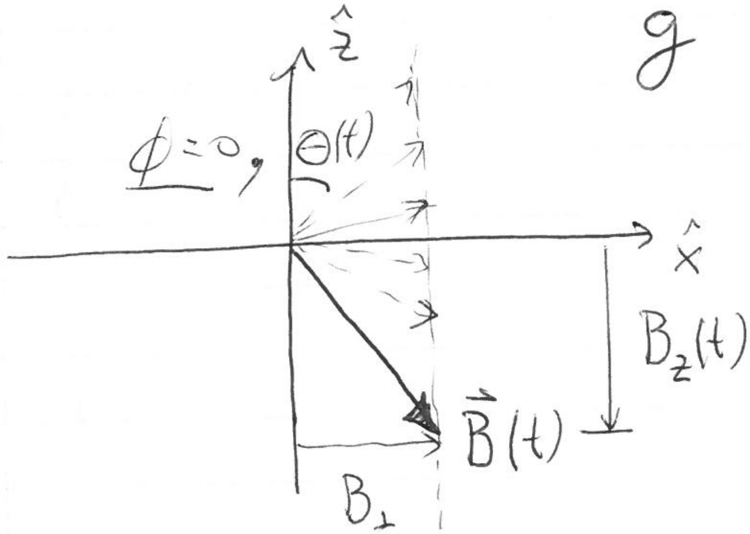
$$H = \begin{pmatrix} -\epsilon(t) & g \\ g & \epsilon(t) \end{pmatrix}, \qquad \epsilon(t) = \lambda t$$

Ex. a single spin in $\vec{B}(t)$ field

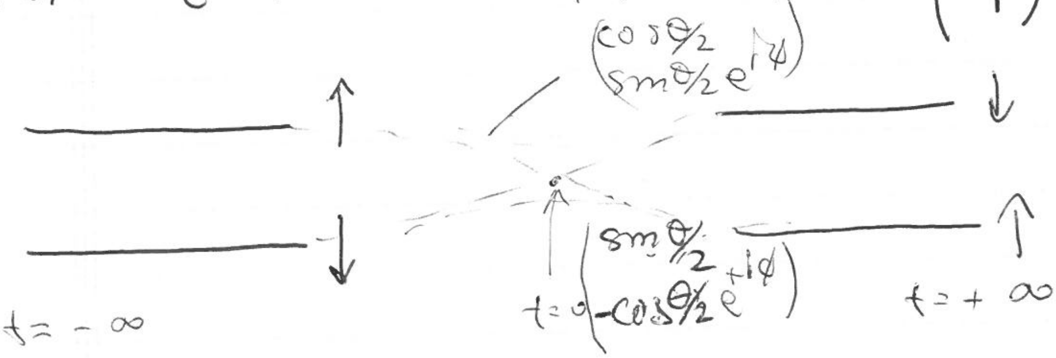
$$\vec{B}(t) = \hat{x} B_\perp + \hat{z} B_z(t)$$

$$\Rightarrow H = -\vec{\mu}\cdot\vec{B}(t) = \underbrace{\mu_B B_\perp}_{g} \sigma^x + \underbrace{\mu_B B_z(t)}_{-\epsilon(t)} \sigma^z$$

$$\left(\mu_B = \frac{e\hbar}{2mc}\right)$$



For $t \to -\infty$ $\quad \psi(t \to -\infty) = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ eigenstate



Complete soln:

Solve time-dependent Sch. Eqn.

$$i\hbar\,\partial_t \begin{pmatrix} \psi_\uparrow(t) \\ \psi_\downarrow(t) \end{pmatrix} = H \begin{pmatrix} \psi_\uparrow \\ \psi_\downarrow \end{pmatrix}$$

$$\left.\begin{aligned} i\hbar\,\partial_t \psi_\uparrow &= -\lambda t\,\psi_\uparrow + g\,\psi_\downarrow \\ i\hbar\,\partial_t \psi_\downarrow &= \lambda t\,\psi_\downarrow + g\,\psi_\uparrow \end{aligned}\right\} ?$$

eliminate $\psi_\downarrow$ (or $\psi_\uparrow$):

$$\frac{1}{g}\left(i\hbar\,\partial_t^2 \psi_\uparrow + \lambda \psi_\uparrow + \lambda t\,\partial_t \psi_\uparrow\right) = \partial_t \psi_\downarrow$$

$$\Rightarrow \frac{i\hbar}{g}\left(i\hbar\,\partial_t^2 \psi_\uparrow + \lambda \psi_\uparrow + \cancel{\lambda t\,\partial_t \psi_\uparrow}\right) =$$

$$= \frac{\lambda t}{g}\left(\cancel{i\hbar\,\partial_t \psi_\uparrow} + \lambda t\,\psi_\uparrow\right) + g\,\psi_\uparrow$$

$$-\frac{\hbar^2}{g}\partial_t^2 \psi_\uparrow + \left(\frac{i\hbar\lambda}{g} - \frac{\lambda^2 t^2}{g} - g\right)\psi_\uparrow = 0$$

$$\frac{2\hbar\lambda}{g}\left[\frac{\hbar}{2\lambda}\partial_t^2 \psi_\uparrow + \left(\frac{2\lambda}{\hbar}\frac{1}{4}t^2 - \frac{i}{2} + \frac{g^2}{2\hbar\lambda}\right)\psi_\uparrow\right] = 0$$

take $t = \underbrace{\sqrt{2\lambda/\hbar}}_{\text{unit of time}}\,\hat{t}$

$$\ddot{\psi}_\uparrow + \left(\tfrac{1}{4}t^2 - \tfrac{i}{2} + \tfrac{1}{2}\alpha\right)\psi_\uparrow = 0$$

$$\ddot{\psi}_\downarrow + \left(\tfrac{1}{4}t^2 + \tfrac{i}{2} + \tfrac{1}{2}\alpha\right)\psi_\downarrow = 0$$

w/ $\alpha = \dfrac{g^2}{\hbar\lambda}$ $[\lambda] = E/t$

$[\hbar\lambda] = E^2 = [g^2]$

dimensionless coupling.

looks like Harmonic oscillator S. Eqn. but w/ $x \to t$ & w/ complex energy.

general solns of $\ddot{y} + (x^2/4 - c)y = 0$

$$y_1(x) = e^{-ix^2/4} M(-ic/2 + 1/4,\ 1/2,\ ix^2/2)$$

$$y_2(x) = x e^{-ix^2/4} M(-ic/2 + 3/4,\ 3/2,\ ix^2/2)$$

even & odd in x, where,

$M(a,b;z)$ is the confluent hypergeom. func. w/ asymptotics:

$$\frac{M(a,b;z)}{\Gamma(b)} = \frac{e^{\pm i\pi a} z^{-a}}{\Gamma(b-a)}\left(1 + O(z^{-1})\right) + \frac{e^z z^{a-b}}{\Gamma(a)}\left(1 + O\left(\tfrac{1}{z}\right)\right)$$

(see J. Levinsen notes)

$\Rightarrow$ general soln

$$\psi_\uparrow(t) = c_1 e^{-it^2/4} M(1/2 + i\alpha/4, 1/2, it^2/2)$$
$$+ c_2 t e^{-it^2/4} M(1 + i\alpha/4, 3/2, it^2/2)$$

$$\psi_\downarrow(t) = c_3 e^{-it^2/2} M(i\alpha/4, 1/2, it^2/2)$$
$$+ c_4 t e^{-it^2/4} M(1/2 + i\alpha/4, 3/2, it^2/2)$$

choose $c_{1,2,3,4}$ s.t. $t \to \pm\infty$

$\psi_\uparrow(t) \to$

Determine $c_{1,2,3,4}$ via initial condit's

$$\lim_{t\to\pm\infty} \psi_\uparrow(t) = e^{it^2/4} (it^2/2)^{i\alpha/4} \sqrt{\pi} \left(\frac{c_1}{\Gamma(1/2 + i\alpha/4)} \pm \frac{c_2}{2\Gamma(1+i\alpha/4)} \left(\frac{i}{2}\right)^{-1/2} \right)$$

$$\psi_\uparrow(t\to-\infty) = 0 \Rightarrow \frac{c_1}{c_2} = \frac{\Gamma(1/2 + i\alpha/4)}{2\Gamma(1+i\alpha/4)} \left(\frac{i}{2}\right)^{-1/2}$$

$$\psi_\downarrow(t) \underset{t\to\pm\infty}{=} e^{-it^2/4} \sqrt{\pi} e^{-\pi\alpha/4} (it^2/2)^{-i\alpha/4} \left(\frac{c_3}{\Gamma(1/2 - i\alpha/4)} \pm \frac{c_4}{2\Gamma(1-i\alpha/4)} i \left(\frac{i}{2}\right)^{-1/2} \right)$$

$|\psi_\downarrow| = 1$ as $t \to -\infty$

$$\Rightarrow \quad 1 = \sqrt{\pi} e^{-\pi\alpha/4} \left(\frac{i}{2}\right)^{-i\alpha/4} \left(\frac{c_3}{\Gamma(1/2 - i\alpha/4)} - \frac{c_4}{2\Gamma(1-i\alpha/4)} i \left(\frac{i}{2}\right)^{-1/2} \right)$$

use Schrod. Eqn for $i\hbar\partial_t \psi_{\uparrow,\downarrow} = \ldots$ to determine c_i's. & evaluate at $t=0$

$$\Rightarrow \quad ic_2 = \sqrt{\frac{\alpha}{2}}\, c_3 \quad ; \quad ic_4 = \sqrt{\frac{\alpha}{2}}\, c_1$$

$\Rightarrow$ Transition rate:

$$|\psi_\uparrow(t)|^2 \underset{t\to\infty}{=} \left| \left(\frac{i}{2}\right)^{i\alpha/4} \left(c_1 \frac{\sqrt{\pi}}{\Gamma(1/2 + i\alpha/4)} + c_2 \frac{\sqrt{\pi}}{2\Gamma(1+i\alpha/4)} \left(\frac{i}{2}\right)^{-1/2} \right) \right|^2$$

$$= \pi^2 \alpha e^{-\pi\alpha/2} \left| \frac{1}{\Gamma(1+i\alpha/4)\Gamma(1/2+i\alpha/4)} \right|^2$$

using $\Gamma(1/2 + iy)\Gamma(1/2 - iy) = \dfrac{\pi}{\cosh \pi y}$ $\qquad (i^{ix} = e^{-\pi x/2})$

$\Gamma(1+iy)\Gamma(1-iy) = \dfrac{\pi y}{\sinh \pi y}$

$$\boxed{|\psi_\uparrow(t)|^2 \underset{t\to+\infty}{=} 1 - e^{-\pi\alpha}} \quad , \quad \alpha = \frac{g^2}{\lambda\hbar}$$

Perturbation theory:

$$\hbar i \dot{\psi}_\uparrow^{(1)} = -\lambda t\, \psi_\uparrow^{(1)} + g\, \psi_\downarrow^{(0)} \qquad \Big| \quad \hbar i \dot{\psi}_\downarrow = \lambda t\, \psi_\downarrow + g\, \psi_\uparrow$$

to lowest order drop $g\psi_\uparrow$

$$\Rightarrow \psi_\downarrow^{(0)} = 1\, e^{-\frac{i\lambda}{\hbar 2} t^2}$$

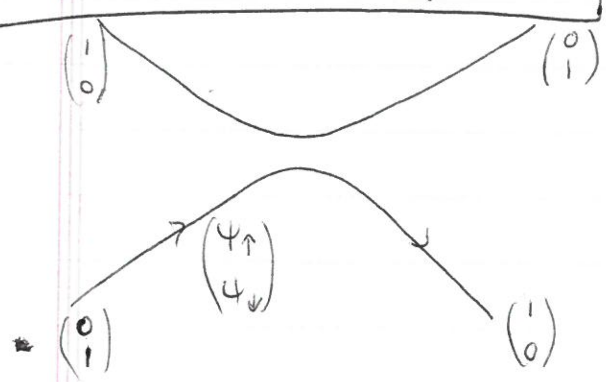
$$\hbar i \psi_\uparrow^{(1)} = -\lambda t\, \psi_\uparrow^{(1)} + g\, e^{-\frac{i\lambda}{2}\frac{t^2}{\hbar}}$$

$$\psi_\uparrow^{(1)}(t) = -\frac{ig}{\hbar}\, e^{\frac{i\lambda}{\hbar 2} t^2} \int_{t_0}^{t} dt'\, e^{-\frac{i\lambda}{\hbar} t'^2}$$

$t_0 \to -\infty \qquad \psi_\uparrow^{(1)}(-\infty) \to 0$

$$\Rightarrow \psi_\uparrow^{(1)}(t \to +\infty) = -\frac{ig}{\hbar}\, e^{i\frac{\lambda}{2\hbar} t^2} \underbrace{\int_{-\infty}^{\infty} dt'\, e^{-i\frac{\lambda}{\hbar} t'^2}}_{\sqrt{\frac{\pi\hbar}{i\lambda}}}$$

$$\Rightarrow \boxed{|\psi_\uparrow^{(1)}|^2 \underset{t\to+\infty}{=} \frac{\pi g^2}{\hbar\lambda}} \simeq \underbrace{1 - e^{-\pi g^2/\hbar\lambda}}_{\text{(L-Z exact)}} \simeq \pi g^2/\hbar\lambda \ \checkmark$$



fast $\lambda \Rightarrow \begin{pmatrix}0\\1\end{pmatrix} \to \begin{pmatrix}0\\1\end{pmatrix}$

with $P_{\downarrow\to\downarrow} \simeq 1$ &

$\begin{pmatrix}0\\1\end{pmatrix} \to \begin{pmatrix}1\\0\end{pmatrix}$

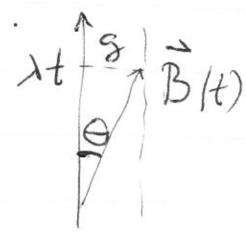
$$P_{\downarrow\to\uparrow} \approx \frac{\pi g^2}{\lambda} \ll 1$$

Landau's "WKB" approach

Adiabatic: $H\,|\hat{n}(t), \sigma\rangle = E_{\sigma}(t)\,|\hat{n}(t), \sigma\rangle$

$\hat{n}(t)$: quantization axis; $\sigma = \pm 1$

$$H = -\vec{\sigma}\cdot\vec{B}$$



$$= \begin{pmatrix} -\lambda t & g \\ g & \lambda t \end{pmatrix}$$

$$E_\sigma = \sigma|\vec{B}| = \sigma\sqrt{\lambda^2 t^2 + g^2} = \sigma\, E(t)$$

eigenstates $U_{\hat{z}\to\hat{n}(t)}\,|\hat{z}, \sigma\rangle$

$$\begin{pmatrix} \psi_\uparrow \\ \psi_\downarrow \end{pmatrix}_+ = U\begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \begin{pmatrix} \psi_\uparrow \\ \psi_\downarrow \end{pmatrix}_- = U\begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix} \xleftarrow[t\to-\infty]{} \begin{pmatrix} \psi_\uparrow \\ \psi_\downarrow \end{pmatrix}_+ = \begin{pmatrix} \cos\theta/2 \\ e^{i\phi}\sin\theta/2 \end{pmatrix}, \quad \begin{pmatrix} \psi_\uparrow \\ \psi_\downarrow \end{pmatrix}_- = \begin{pmatrix} -\sin\theta/2 \\ e^{i\phi}\cos\theta/2 \end{pmatrix} \xrightarrow[t\to-\infty]{} \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

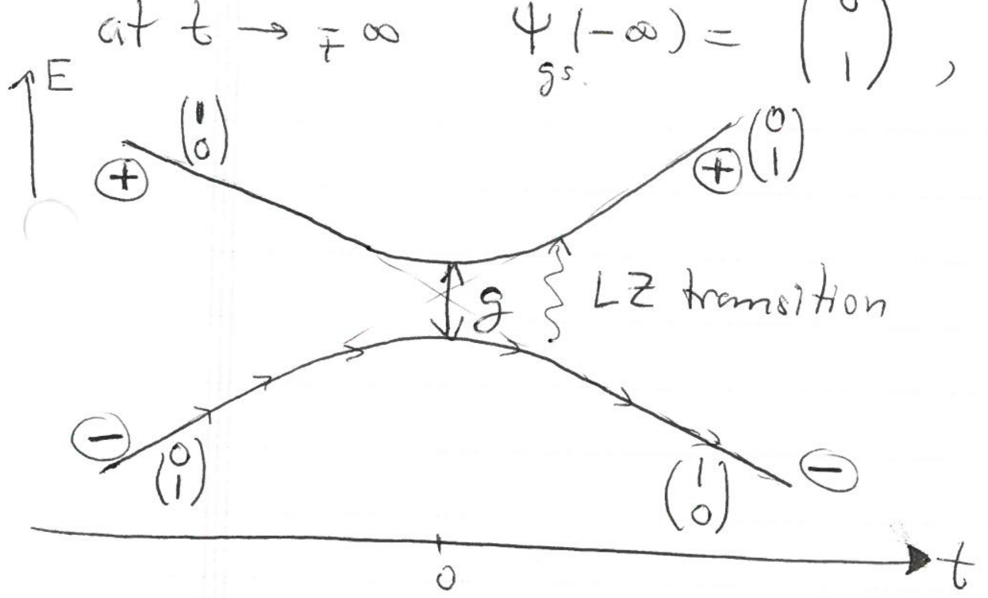
$$\cos\theta = \frac{-\lambda t}{E(t)} = \cos^2\theta/2 - \sin^2\theta/2 = 1 - 2\sin^2\theta/2$$

$$\Rightarrow \sin\theta/2 = \sqrt{\tfrac{1}{2}(1-\cos\theta)} = \sqrt{\tfrac{1}{2}\left(1 + \frac{\lambda t}{\sqrt{\lambda^2 t^2 + g^2}}\right)}$$

$$\cos\theta/2 = \sqrt{\tfrac{1}{2}(1+\cos\theta)} = \sqrt{\tfrac{1}{2}\left(1 - \frac{\lambda t}{\sqrt{\lambda^2 t^2 + g^2}}\right)}$$

(5.10h)

at $t \to \mp\infty$ $\quad \Psi_{gs}(-\infty) = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$, $\quad \Psi_{gs}(+\infty) = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$



$\lambda \to 0 \Rightarrow$ adiabatically follow $|-\rangle$ state

at small λ rate, small but finite $P_{\ominus \to \oplus} = ?$

$$H(|t| \to \infty) \simeq \begin{pmatrix} -\lambda t & 0 \\ 0 & \lambda t \end{pmatrix} \Rightarrow \begin{pmatrix} 0 \\ 1 \end{pmatrix} \ \& \ \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$ g.states for $t \to \mp\infty$, respectively.

<u>note</u>: For t real $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$ evolves into $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$

as t goes from $-\infty$ to $+\infty$ (keeping $\sqrt{t^2\lambda^2+g^2} > 0$)

For nonzero λ WKB breaks down for $t \simeq 0$

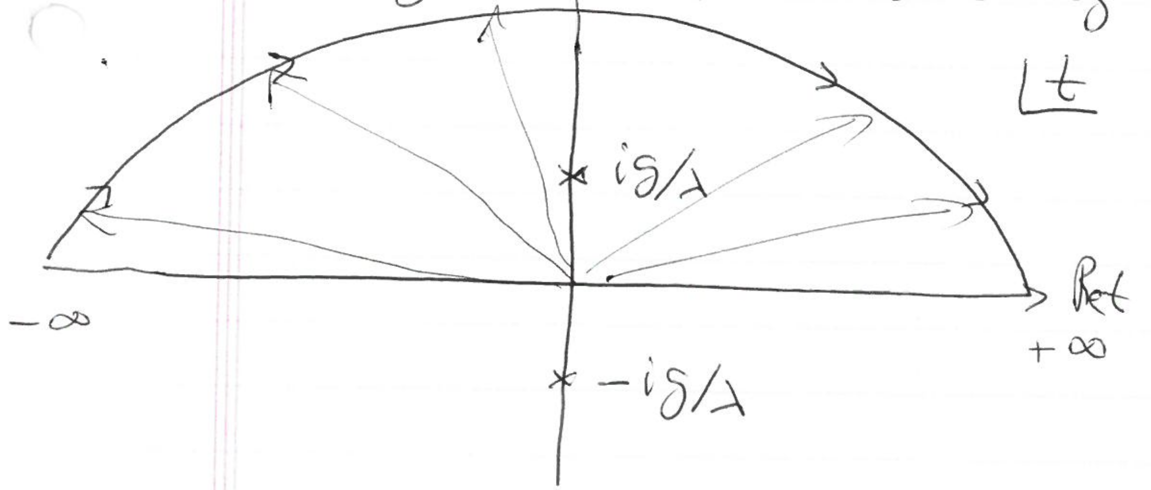
$$\Psi(t) = \Psi_-(t)\, e^{-\frac{i}{\hbar}\int_{-\infty}^{t} dt'\, E_-(t')} = \Psi_-(t)\, e^{\frac{i}{\hbar}\underbrace{\int_{-\infty}^{t} dt' \sqrt{\lambda^2 t'^2 + g^2}}_{\text{real if real integral}}}$$

$\Rightarrow$ just a phase factor $\Rightarrow$ no transition from $\ominus$ to $\oplus$!

this WKB approx misses imaginary part of phase since it breaks down for small t.

Allow $\int_{-\infty}^{t} dt' \sqrt{\lambda^2 t'^2 + g^2}$ to be a complex fnc of $t \in$ complex plane.

For t complex & <u>far away</u> from $t_* = \pm i g/\lambda$
then WKB is valid since strong complex $\vec{B}$ field!



So WKB is exact for contour integral on ∞ circle

$$\oint_{-\infty}^{\infty} dt\, \sqrt{\lambda^2 t^2 + g^2} \simeq \int_{-\infty}^{\infty} dt \left(\lambda t + \frac{1}{2}\frac{g^2}{\lambda t} \right) = \frac{1}{2}\lambda t^2$$

$$+ \frac{g^2}{2\lambda} \underbrace{\oint_{-\infty}^{\infty} \frac{dt}{t}}_{i\pi}$$

$+ \dots$ vanish on great circle

$(g=0)$ free evolution $\int E$

$t = |t| e^{i\phi}$

$\frac{dt}{t} = \frac{\cancel{|t|}}{\cancel{|t|}}\, i\, d\phi$

$$\Rightarrow \Psi(t \to +\infty) = \underbrace{\Psi_-(t \to +\infty)}_{\text{taking negative } \sqrt{\ }} e^{\frac{i}{2}\frac{\lambda t^2}{\hbar}} e^{-\frac{\pi g^2}{2\lambda\hbar}}$$

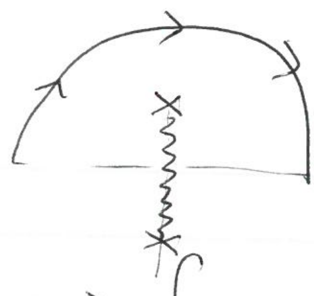
$$\Psi_-(t \to \infty) = \Psi_+ = \begin{pmatrix} 0 \\ 1 \end{pmatrix} !$$

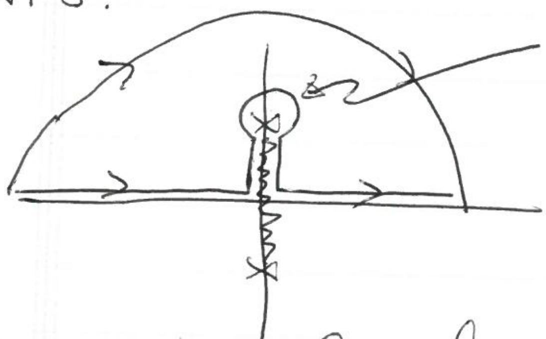
$$\Rightarrow \boxed{(1 \ \ 0)^{+} \cdot \Psi(t \to +\infty) = e^{-\pi g^2/\lambda\hbar} = P_{\ominus \to \oplus}}$$

$\Leftarrow$ prob to trans to $\oplus$ state.

$$\boxed{P_{\ominus \to \ominus} = 1 - e^{-\pi g^2/\lambda\hbar}}$$

$\leftarrow$ prob. to stay in $\ominus$ state

Equivalently,  can be deformed to be along real axis.



$\oint f = 0$

the integral along real axis just gives inconsequential phase. The trans. prob. comes from

$$\sqrt{e^{i2\pi}} = -1$$

$$\phi = i\int_0^{g/\lambda} d\tau \sqrt{g^2-\lambda^2\tau^2} + i\int_{g/\lambda}^{0} d\tau\,(-1)\sqrt{g^2-\lambda^2\tau^2}$$

$$= 2i\int_0^{g/\lambda} d\tau \sqrt{g^2-\lambda^2\tau^2}$$

$$e^{\frac{i}{\hbar}\int_{-\infty}^{\infty} dt\, E(t)} = e^{-\frac{g^2}{\lambda\hbar}\, 2\cdot\frac{\pi}{4}} = e^{-\frac{g^2\pi}{2\lambda\hbar}}$$

Perturbation theory for $\hat{U}$

A. Schrodinger picture:

$$i\hbar\partial_t |\psi_s(t)\rangle = H_s|\psi_s(t)\rangle \Rightarrow |\psi_s(t)\rangle = U_s(t)|\psi_s(0)\rangle$$

$$P(n,t) = |\underbrace{\langle n|\psi_s(t)\rangle}_{c_n(t)}|^2 = |\langle n|U_s(t)|\psi_s(0)\rangle|^2$$

prob. of being in state $|n\rangle$ after evolution for time t from state $|\psi_s(0)\rangle$

$U_s(t)$ – Schrodinger's evolution operator.

- If H_s is t-independent

$$\hat{U}_s(t) = e^{-\frac{i}{\hbar}H_s t}$$

- If $H_s(t)$ but $[H_s(t), H_s(t')] = 0$

$$\Rightarrow \hat{U}_s(t) = e^{-\frac{i}{\hbar}\int_0^t H_s(t')dt'}$$

- If $[H_s(t), H_s(t')] \neq 0$

$$\Rightarrow \hat{U}_s(t) = T\left[e^{-\frac{i}{\hbar}\int_0^t H_s(t')dt'}\right]$$

time-ordered $\Leftrightarrow$ operators at later time appear to the left

Note: $\hat{U}^{+}\hat{U} = \mathbb{1}$

$$\hat{U}(t_3, t_2)\,\hat{U}(t_2, t_1) = \hat{U}(t_3, t_1)$$

$$\hat{U}(t_1, t_1) = \mathbb{1}$$

$$\hat{U}^{+}(t_2, t_1) = \hat{U}(t_1, t_2)$$

suppose

$$H_s = H_0 + \underbrace{H_1}_{\text{perturbation}}, \qquad [H_0, H_1] \neq 0 \text{ generally.}$$

$$C_n(t) = \langle n|\, e^{-\frac{i}{\hbar}\int_0^t H_0\,dt' - \frac{i}{\hbar}\int_0^t H_1\,dt'} \,|i\rangle$$

$$\neq \langle n|\, e^{-\frac{i}{\hbar}\int^t H_0}\, e^{-\frac{i}{\hbar}\int^t H_1} \,|i\rangle$$

otherwise could Taylor expand in $\int^t H_1$, obtaining perturbation series for $C_n(t)$.

... but can do this in the interaction repres.!

B. Interaction picture

$$|\psi_s(t)\rangle = e^{-\frac{i}{\hbar}\int^t (H_0 + H_1)\,dt'}\,|\psi_s(0)\rangle$$

$$= \underbrace{e^{-\frac{i}{\hbar}\int^t H_0\,dt'}}_{U_s^0(t)}\ \underbrace{e^{+\frac{i}{\hbar}\int^t H_0\,dt'}\, e^{-\frac{i}{\hbar}\int^t (H_0+H_1)\,dt'}\,|\psi_s(0)\rangle}_{\equiv |\psi_I(t)\rangle}$$

$$|\psi_s(t)\rangle = U_s^0(t)\,|\psi_I(t)\rangle$$

$$|\psi_S(0)\rangle = |\psi_I(0)\rangle$$

$$|\psi_I(t)\rangle = U_I(t)|\psi_I(0)\rangle$$

$$U_I(t) = e^{\frac{i}{\hbar}\int^t H_0 dt'} e^{-\frac{i}{\hbar}\int^t H dt'} = U_S^{0+}(t)\, U_S(t)$$

<u>Note</u>: if $[H_1, H_0] = 0$

$$\Rightarrow \quad U_I(t) = e^{-\frac{i}{\hbar}\int^t H_1 dt'}$$

Sch. Eqn in I. repres.:

$$|\psi_S(t)\rangle = U_S^0(t)|\psi_I(t)\rangle$$

$$i\hbar\partial_t|\psi_S(t)\rangle = i\hbar(\partial_t U_S^0)|\psi_I(t)\rangle$$

$$+ U_S^0\, i\hbar\partial_t|\psi_I(t)\rangle = (H_0 + H_1)U_S^0|\psi_I(t)\rangle$$

$$U_S^0\left(\cancel{H_0|\psi_I(t)\rangle} + i\hbar\partial_t|\psi_I(t)\rangle = (\cancel{H_0} + H_1)U_S^0|\psi_I(t)\rangle\right.$$

$$\boxed{i\hbar\partial_t|\psi_I(t)\rangle = H_I'(t)|\psi_I(t)\rangle}$$

where, $\underline{H_I'(t) = U_S^{0+}(t)\, H_S'\, U_S^0(t)}$

$$\Rightarrow \underline{i\hbar\partial_t U_I(t) = H_I'(t)\, U_I(t)}$$

since in general $[H_I'(t), H_I'(t')] \neq 0 \Rightarrow \underline{U_I = T\left[e^{-\frac{i}{\hbar}\int^t dt' H_I'(t')}\right]}$

5.14

Soln to: $i\hbar\,\partial_t U_I = H_I'(t)\, U_I$

(a) iteration of integral eqn.:

$$\hat{U}_I^{(i+1)}(t) = \mathbb{1} - \frac{i}{\hbar}\int_0^t dt'\, H_I'(t')\, U_I^{(i)}(t')$$

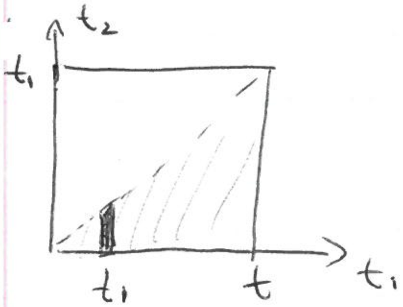
$$\hat{U}_I^{(0)} = \mathbb{1}$$

$$\hat{U}_I^{(1)} = \mathbb{1} - \frac{i}{\hbar}\int_0^t dt_1\, H_I'(t_1)$$

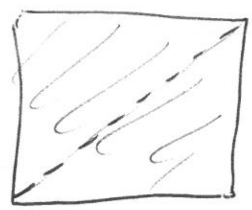
$$\hat{U}_I^{(2)} = \mathbb{1} + \left(\frac{-i}{\hbar}\right)^1 \int_0^t dt_1\, H_I'(t_1) + \left(\frac{-i}{\hbar}\right)^2 \int_0^t dt_1\, H_I'(t_1) \int_0^{t_1} dt_2\, H_I'(t_2)$$

$\vdots$

$$\boxed{\hat{U}_I = \mathbb{1} + \left(\frac{-i}{\hbar}\right)\int_0^t dt_1\, H_I'(t_1) + \left(\frac{-i}{\hbar}\right)^2 \int_0^t dt_1\, H_I'(t_1)\int_0^{t_1} dt_2\, H_I'(t_2) + \left(\frac{-i}{\hbar}\right)^3 \int_0^t dt_1\, H_I'(t_1)\int_0^{t_1} dt_2\, H_I'(t_2)\int_0^{t_2} dt_3\, H_I'(t_3) + \dots}$$



$= \frac{1}{2!}$



$$\hat{U}_I = \mathbb{1} + \left(\frac{-i}{\hbar}\right)\int_0^t dt_1\, H_I'(t_1) + \frac{1}{2!}\left(\frac{-i}{\hbar}\right)^2 \int_0^t dt_1 \int_0^t dt_2\, \mathcal{T}\left[H_I'(t_1) H_I'(t_2)\right]$$

$$+ \frac{1}{3!}\left(\frac{-i}{\hbar}\right)^2 \int_0^t dt_1 \int_0^t dt_2 \int_0^t dt_3\, \mathcal{T}\left[H_I'(t_1) H_I'(t_2) H_I'(t_3)\right] + \dots$$

$$\Rightarrow \boxed{\hat{U}_I(t_0) = \mathcal{T}\left[e^{-\frac{i}{\hbar}\int_0^t dt'\, H_I'(t)}\right]}$$

(b) Formal soln: $i\hbar \partial_t U_I = H_I'(t) U_I$

$$U_I(t) = T\left[e^{-\frac{i}{\hbar}\int_0^t dt' H_I'(t')}\right]$$

$$= \mathbb{1} + \left(\frac{-i}{\hbar}\right)\int_0^t dt_1\, H_I'(t_1) + \frac{1}{2!}\left(\frac{-i}{\hbar}\right)\int_0^t dt_1 \int_0^t dt_2\, T[H_I'(t_1) H_I'(t_2)]$$

$$+ \dots$$

$$i\hbar\partial_t U_I(t) = H_I'(t)\left(\mathbb{1} + \left(\frac{-i}{\hbar}\right)\int^t dt_1\, H_I'(t_1) + \dots\right)$$

$$= H_I'(t) U_I(t)$$

Note: $\partial_t\left[\int^t H_I(t_1) \int^t H_I(t_2)\right]$

$$= H_I(t)\int^t H_I(t_2) + \int^t H_I(t_1)\, H_I(t)$$

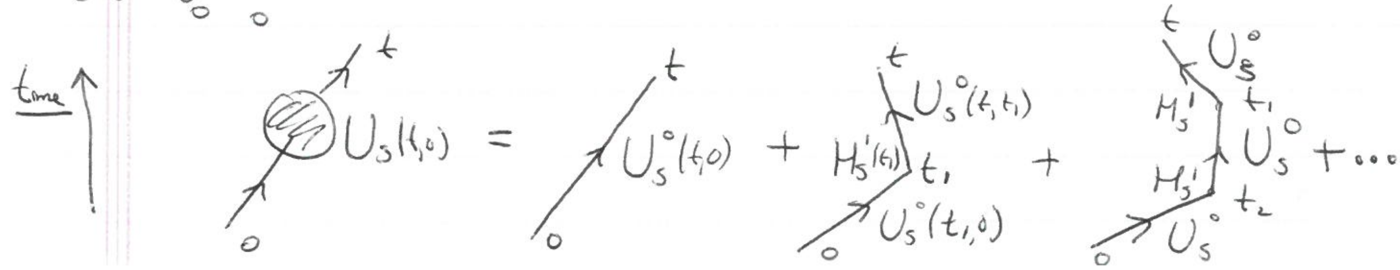
$$\neq 2H_I(t)\int^t H_I(t')$$

this is why we need $T[\dots]$ operator.

$U_s(t,0) = U_s^\circ(t,0)\, U_I(t,0)$, $\quad H_I'(t) = U_s^{\circ\dagger}(t,0)\, H'(t)\, U_s^\circ(t,0)$

$$\Rightarrow U_s(t,0) = U_s^\circ(t,0) + \left(\frac{-i}{\hbar}\right)\int_0^t U_s^\circ(t,t_1)\, H_s'(t_1)\, U_s^\circ(t_1,0)\, dt_1$$

$$+ \left(\frac{-i}{\hbar}\right)^2 \int_0^t \int_0^{t_1} U_s^\circ(t,t_1)\, H_s'(t_1)\, U_s^\circ(t_1,t_2)\, H_s'(t_2)\, U_s^\circ(t_2,0)\, dt_1 dt_2$$



Perturbative expression for $c_f(t)$:

$$|\Psi_s(t)\rangle = U_s(t,0)|i_s^0\rangle = U_s^0(t,0)\,U_I(t,0)|i_s^0\rangle$$

$$\langle f_s^0|\Psi_s(t)\rangle = e^{-\frac{i}{\hbar}E_f^0 t}\langle f_s^0|U_I(t,0)|i_s^0\rangle$$

$$= \delta_{fi}\, e^{-\frac{i}{\hbar}E_f^0 t} + \left(\frac{-i}{\hbar}\right) e^{-\frac{i}{\hbar}E_f^0 t}\int_0^t e^{\frac{i}{\hbar}(E_f^0-E_i^0)t_1}\langle f_s^0|H_s'(t_1)|i_s^0\rangle$$

$$+ \left(\frac{-i}{\hbar}\right)^2 e^{-\frac{i}{\hbar}E_f^0 t}\sum_n\int_0^t e^{\frac{i}{\hbar}E_f^0 t_1}\langle f_s^0|H_s'(t_1)|n_s\rangle\langle n_s|H_s'(t_2)|i_s^0\rangle \cdot$$

$$\cdot\, e^{-\frac{i}{\hbar}E_n^0(t_1-t_2)-\frac{i}{\hbar}E_i^0 t_2}\, dt_1\, dt_2 + \dots$$

$$d_f(t) = \delta_{fi} + \left(\frac{-i}{\hbar}\right)\int_0^t \langle f_s^0|H_s'(t_1)|i_s^0\rangle\, e^{\frac{i}{\hbar}(E_f^0-E_i^0)t_1}\, dt_1$$

$$+\left(\frac{-i}{\hbar}\right)^2\sum_{n_s}\int_0^t\int_0^{t_1} e^{\frac{i}{\hbar}(E_f^0-E_n^0)t_1}\langle f_s^0|H_s'(t_1)|n_s\rangle\langle n_s|H_s'(t_2)|i_s^0\rangle\cdot$$

$$\cdot\, e^{\frac{i}{\hbar}(E_n^0-E_i)t_2}\, dt_1\, dt_2 + \dots$$

$$C_f(t) = \delta_{fi}\, e^{-\frac{i}{\hbar}E_f(t-t_0)} + \left(\frac{-i}{\hbar}\right)\int_{t_0}^t dt_1\, e^{-\frac{i}{\hbar}E_f(t-t_1)}\langle f|H_1(t_1)|i\rangle e^{-\frac{i}{\hbar}E_i(t_1-t_0)}$$

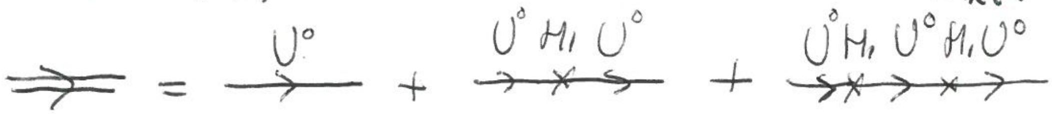
$$+\sum_n\left(\frac{-i}{\hbar}\right)^2\int_{t_0}^t dt_1\int_{t_0}^{t_1} dt_2\, e^{-\frac{i}{\hbar}E_f(t-t_1)}\langle f|H_1(t_1)|n\rangle e^{-\frac{i}{\hbar}E_n(t_1-t_2)}\langle n|H_1(t_2)|i\rangle e^{-\frac{i}{\hbar}E_i(t_2-t_0)} + \dots$$

$$C_f = \langle f|\hat U(t)|i\rangle = U_{fi}^0(t) + \left(\frac{-i}{\hbar}\right)\int_{t_0}^t dt_1 \sum_{n,m} U_{fn}^0(t-t_1)\, H'_{nm}(t_1)\, U^0_{mi}(t_1-t_0)$$

$$+\left(\frac{-i}{\hbar}\right)^2\int_{t_0}^t dt_1\int_{t_0}^{t_1}dt_2\sum_{n,m,l,k} U^0_{fn}(t-t_1)\, H'_{nm}(t_1)\, U^0_{ml}(t_1-t_2)\, H'_{lk}(t_2)\cdot$$

$$\cdot\, U^0_{ki}(t_2-t_0)$$

$+\dots$



$+\dots$

(c) Path integral perturbation series for $U(r,r';t)$

$$U(r,r';t,t_0) = \int_{r(t_0)=r'}^{r(t)=r} \mathcal{D}r \; e^{\frac{i}{\hbar}\underbrace{S[r(t)]}_{S_0 + S_1}}$$

$$= \int \mathcal{D}r \; e^{\frac{i}{\hbar}\int_{t_0}^{t} dt' L_0} \; e^{-\frac{i}{\hbar}\int_{t_0}^{t} dt_1 H_1[t_1, r(t_1)]}$$

$$= \int \mathcal{D}r \; e^{\frac{i}{\hbar}\int_{t_0}^{t} dt' L_0} \Big[1 + \left(\frac{-i}{\hbar}\right)\int_{t_0}^{t} dt_1 H_1[r(t_1), t_1]$$

$$+ \frac{1}{2!}\left(\frac{-i}{\hbar}\right)^2 \int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 \; H_1[r(t_1), t_1] \, H_1[r(t_2), t_2]$$

$$+ \ldots \Big]$$

$$= \int_{r(t_0)}^{r(t)} \mathcal{D}r \; e^{\frac{i}{\hbar}\int_{t_0}^{t} dt' L_0} + \left(\frac{-i}{\hbar}\right)\int_{t_0}^{t} dt_1 \int_{r(t_1)}^{r(t)} \mathcal{D}r \; e^{\frac{i}{\hbar}\int_{t_1}^{t} dt' L_0} \; H_1[r(t_1), t_1] \times$$

$$\times \int_{r(t_0)}^{r(t_1)} \mathcal{D}r \; e^{\frac{i}{\hbar}\int_{t_0}^{t_1} dt' L_0} + \left(\frac{-i}{\hbar}\right)^2 \frac{1}{2!} \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \int_{r(t_1)}^{r(t)} \mathcal{D}r \; e^{\frac{i}{\hbar}\int_{t_1}^{t} L_0} \; H_1[r(t_1), t_1]$$

$$\times \int_{r(t_2)}^{r(t_1)} \mathcal{D}r \; e^{\frac{i}{\hbar}\int_{t_2}^{t_1} L_0} \; H_1[r(t_2), t_2] \int_{r(t_0)}^{r(t_2)} \mathcal{D}r \; e^{\frac{i}{\hbar}\int_{t_0}^{t_2} L_0} \times 2!$$

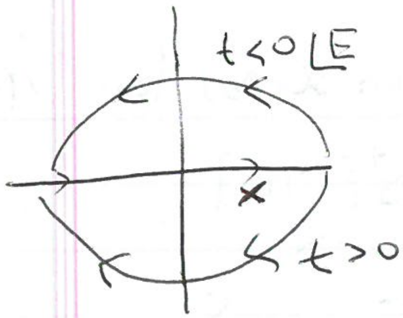
2 orderings in time $t_1 > t_2$
$t_1 < t_2$

$+ \ldots$

$$U(r,r';t,t_0) = U_0(r,r';t-t_0) + \left(\frac{-i}{\hbar}\right)\int_{t_0}^{t} dt_1 \int dr_1 \, U_0(r,r_1,t-t_1)$$

$$\times H_1(r_1,t_1) \, U_0(r_1,r';t_1-t_0) + \ldots$$

<u>Note</u>: automatically time-ordered in P-I approach!



$$U_>(t) = \int_{-\infty}^{\infty} dE \, \frac{e^{-iEt}}{E - H + i\varepsilon} \propto \Theta(t).$$

$$\propto e^{-iHt} e^{-\varepsilon t}$$

T-matrix:

$$U = U_0 + U_0 H_1 U_0 + U_0 H_1 U_0 H_1 U_0$$

$$= U_0 + U_0 H_1 U = U_0(\mathbb{1} + \underbrace{H_1 U}_{T U_0})$$

$$U - U_0 = T U_0 = H_1 U$$

$$\Rightarrow \quad T = \cancel{U_0^{-1}}(H_1)(U_0 + U_0 H_1 U_0 + \dots)U_0^{+}$$

$$T = H_1 + H_1 U_0 H_1 + H_1 U_0 H_1 U_0 H_1 + \dots$$

$$= H_1 + H_1 U_0 T$$

$$(1 - H_1 U_0) T = H_1 \quad \Rightarrow \quad \boxed{T \equiv \frac{H_1}{1 - H_1 U_0}}$$

$$\boxed{\equiv (1 - H_1 U_0)^{-1} H_1}$$

(d) Dyson's expansion for t-independent H in ω space

$$\hat{U}_{\text{Retarded}}(t) = e^{-\frac{i}{\hbar}Ht - \frac{\varepsilon}{\hbar}t}\,\Theta(t), \quad \text{causal evolution}$$

$$U_R(E) \quad FT(\hat{U}_R(t)) = \int^{\infty} dt\, e^{-\frac{i}{\hbar}Ht}\, e^{\frac{i}{\hbar}\underbrace{(E+i\varepsilon)}_{E}t}$$

$$U_A(t) = e^{-\frac{i}{\hbar}Ht_0}\, e^{+\frac{\varepsilon}{\hbar}t}\,\Theta(-t), \quad \hat{U}_A(E) = \hat{U}_R^{*}(E) = \hat{U}_R(E^{*})$$

$$\hat{U}(E) = \frac{+i\hbar}{E - H} = \frac{i\hbar}{E - H_0 - H_1} = i\hbar\left[E - H_0 - H_1\right]^{-1}$$

$$= i\hbar\left[(E - H_0)(1 - (E - H_0)^{-1}H_1)\right]^{-1}$$

$$= i\hbar\left[1 - (E - H_0)^{-1}H_1\right]^{-1}\left[E - H_0\right]^{-1}$$

$$= i\hbar\left[\frac{1}{E - H_0} + \frac{1}{E - H_0}H_1\frac{1}{E - H_0} + \right.$$

$$\left. + \frac{1}{E - H_0}H_1\frac{1}{E - H_0}H_1\frac{1}{E - H_0} + \ldots\right]$$

$$\hat{U}(E) = i\hbar\left[\hat{U}_0(E) + \hat{U}_0(E)\hat{H}_1\hat{U}_0(E) + \right.$$

$$\left. + \hat{U}_0(E)\hat{H}_1\hat{U}_0(E)\hat{H}_1 U_0(E) + \ldots\right]$$

$$= \hat{U}_0(t - t_0) + \left(\frac{-i}{\hbar}\right)\int \hat{U}_0(t - t_1)\hat{H}_1\hat{U}_0(t_1 - t_0) + \ldots$$

Note:

$\frac{d}{dt}|d_f(t)|^2$ at $\omega = 0$ 1^{st} & 2^{nd} order can interfere

$$\equiv R_{i\to f}^{(\omega=0)} = \frac{2\pi}{\hbar}\left| H'_{fi} + \sum_{n\neq i} \frac{H'_{fn}H'_{ni}}{E_i - E_n}\right|^2 \delta(E_f - E_i)$$

at $\omega \neq 0$ no interference between 1 & 2 photon absorption

$$\Rightarrow R_{i\to f}^{(\omega)} = \frac{2\pi}{\hbar}|H'_{fi}|^2\delta(E_f - E_i - \hbar\omega)$$

$$+ \frac{2\pi}{\hbar}\left|\sum_{\substack{n\neq i\\ \neq f}} \frac{H'_{fn}H'_{ni}}{E_n - E_i - \hbar\omega}\right|^2 \delta(E_f - E_i - 2\hbar\omega)$$

Note: only included absorption terms. $e^{-i\omega t}$

there are also emission terms $e^{+i\omega t}$

which are important for stimulated emission $f \to i$

same

$$\Rightarrow R_{f\to i}^{(\omega)\ 2^{nd}\text{ order emission}} = \frac{2\pi}{\hbar}\underbrace{\left|\sum_{n\neq f} \frac{H'_{in}H'_{nf}}{E_n - E_f + \hbar\omega}\right|^2}_{\left|\sum_{\substack{n\neq f\\ \neq i}} \frac{(H'_{fn}H'_{ni})^*}{E_n - E_i - \hbar\omega}\right|^2} \delta(\underbrace{E_i - E_f + 2\hbar\omega}_{E_f - E_i - 2\hbar\omega})$$

✓

$$\Rightarrow R_{f\to i} = R_{i\to f}$$

✓ same!

Fermi golden rule to higher order

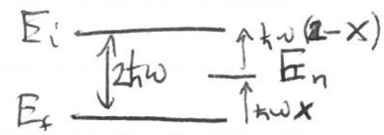
$$d_{f}(t) \underset{f\neq i}{=} \left(\frac{-i}{\hbar}\right)\int_0^t \langle f_s^0 | H_s'(t_1) | i_s^0\rangle e^{\frac{i}{\hbar}(E_f^0-E_i^0)t_1}\, dt_1$$

$$\underbrace{+\left(\frac{-i}{\hbar}\right)^2\sum_n\int_0^t\int_0^{t_1} e^{\frac{i}{\hbar}(E_f^0-E_n^0)t_1}\langle f_s^0|H_s'(t_1)|n_s^0\rangle\langle n_s^0|H_s'(t_2)|i_s^0\rangle e^{\frac{i}{\hbar}(E_n^0-E_i^0)t_2}\, dt_1\, dt_2}_{\text{focus on this correction.}}$$

$$d_f^{(2)}(t) = \left(\frac{-i}{\hbar}\right)^2\sum_n\int_0^t dt_1\, e^{\frac{i}{\hbar}(E_f^0-E_n^0)t_1}\frac{\langle f_s^0|H_s'|n_s^0\rangle e^{-i\omega t_1}}{(i/\hbar)(E_n^0-E_i^0-\hbar\omega)}\left(e^{\frac{i}{\hbar}(E_n^0-E_i^0-\hbar\omega)t_1}-1\right)\cdot\langle n_s^0|H_s'|i_s^0\rangle$$

$$= \left(-\frac{i}{\hbar}\right)\sum_n\int_0^t dt_1\left[e^{\frac{i}{\hbar}(E_f^0-E_i^0)t_1}\frac{\langle f_s|H_s'|n_s\rangle\langle n_s|H_s'|i_s\rangle}{(E_n-E_i-\hbar\omega)}e^{-2i\omega t_1}\right.$$

$$\left. - e^{\frac{i}{\hbar}(E_f-E_n)t_1}\, e^{-i\omega t_1}\frac{\langle\quad\rangle\langle\quad\rangle}{E_n-E_i-\hbar\omega}\right]$$



oscillates, vanish for $E_f \neq E_n + \hbar\omega$, drop.
$\neq E_i$

$$\boxed{\frac{d}{dt}|d_f(t)|^2 = \frac{2\pi}{\hbar}\left(\underbrace{|H'_{fi}|^2\,\delta(E_f-E_i-\hbar\omega)}_{\text{1 photon absorption}} + \left|\sum_n\frac{H'_{fn}H'_{ni}}{(\hbar\omega+E_i-E_n)}\right|^2\underbrace{\delta(E_f-E_i-2\hbar\omega)}_{\text{2 photon absorption}}\right) = R_{i\to f}.}$$

<u>Note</u>: "quanta" of energy $\hbar\omega$ is absorbed from sinusoidal source, without limit (cf classical)

Detailed balance $\dfrac{R_{i\to f}}{\rho(E_f)} = \dfrac{R_{f\to i}}{\rho(E_i)}$

Energy shifts & Decay widths
(Relation to TIPT)

Turn on slowly $H_1(t) = e^{t/\tau} H_1$ in far past

$f \neq i$

$$d_f(t) \simeq \frac{-i}{\hbar} H'_{fi} \lim_{t_0 \to -\infty} \int_{t_0}^{t} e^{t_1/\tau} e^{i\omega_{fi} t_1} \, dt_1$$

$$= \frac{-i}{\hbar} \frac{e^{t/\tau + i\omega_{fi} t}}{i\omega_{fi} + \frac{1}{\tau}} H'_{fi}$$

$$|d_f(t)|^2 \simeq \frac{|H'_{fi}|^2}{\hbar^2} \frac{e^{2t/\tau}}{\omega_{fi}^2 + 1/\tau^2}$$

$$\frac{d}{dt}\left(|d_f(t)|^2\right) = R_{i\to f}(t) = \frac{2|H'_{fi}|^2 (1/\tau)}{\hbar^2\left(\omega_{fi}^2 + \frac{1}{\tau^2}\right)}$$

$\frac{d}{dt}$ (const. part from t-indep. p.t / adiabatic) $= 0$

i.e. this "kills" the real part of $|d_f|^2 \neq 0$ due to H_1. What remains is the imaginary part i.e. decay width $\Rightarrow$ Fermi Golden Rule at $\omega = 0$

$$R_{i\to f} \xrightarrow[\tau \to \infty]{} \left(\frac{2\pi}{\hbar}\right) |H'_{fi}|^2 \, \delta(E_f - E_i)$$

What happens to $d_i(t)$?

$$d_i^{(1)} = \frac{-i}{\hbar} H'_{ii} \int_{-\infty}^{t} e^{t'/\tau} dt' = -\frac{i}{\hbar/\tau} e^{t/\tau} H'_{ii}$$

$$d_i^{(2)} = \left(\frac{-i}{\hbar}\right)^2 \sum_n |H'_{ni}|^2 \int_{-\infty}^{t} dt' \, e^{i\omega_{in} t' + t'/\tau} \frac{e^{i\omega_{ni} t' + t'/\tau}}{i(\omega_{ni} - i/\tau)}$$

$$\Rightarrow d_i \simeq 1 - \frac{i}{\hbar/\tau} H'_{ii} e^{t/\tau} + \left(\frac{-i}{\hbar}\right)^2 |H'_{ii}|^2 \frac{e^{2t/\tau}}{2/\tau^2} + \left(\frac{-i}{\hbar}\right) \sum_{n \neq i} \frac{|H'_{ni}|^2 e^{2t/\tau}}{\frac{2}{\tau}(E_i - E_n + i\hbar/\tau)}$$

$$\Rightarrow \frac{\dot{d}_i}{d_i} \simeq \underbrace{\frac{-i}{\hbar} H'_{ii} + \left(\frac{-i}{\hbar}\right) \sum_{n \neq i} \frac{|H'_{ni}|^2}{E_i - E_n + i\hbar/\tau}}_{-\frac{i}{\hbar}\Delta_i = \text{constant}} + \cdots \Rightarrow d_i(t) = 1 \, e^{-\frac{i}{\hbar}\Delta_i t}$$

$$\Rightarrow |i_s(t)\rangle = e^{-\frac{i}{\hbar}(\Delta_i + E_i^0)t} |i\rangle$$

$$\Rightarrow \Delta_i = H'_{ii} + \sum_{n \neq i} \frac{|H'_{ni}|^2}{E_i - E_n + i\hbar/\tau}$$

$$= \underbrace{\Delta E_i}_{\text{energy shift due to perturbation}} + i\underbrace{\Gamma_i}_{\sum_n \hbar R_{i\to n}}/2$$

Using $\lim_{\varepsilon \to 0} \frac{1}{x + i\varepsilon} = P\frac{1}{x} - i\pi\delta(x)$

$$\Rightarrow \Delta E_i = H'_{ii} + P\sum_{n \neq i} \frac{|H'_{ni}|^2}{E_i - E_n}$$

rate out of i into any state n.

$$\frac{\Gamma_i}{\hbar} = \frac{2\pi}{\hbar} \sum_{n \neq i} |V_{ni}|^2 \delta(E_i - E_n) \quad !$$

$$d_i(t) = e^{-\frac{i}{\hbar}[(\mathrm{Re}\,\Delta_i)t] - \frac{1}{\hbar}|\mathrm{Im}\,\Delta_i|t}$$

decays due to transitions $i \to n$.

<u>Note</u>: $|c_i|^2 + \sum_{n \neq i} |c_n|^2 = (1 - \Gamma_i t/\hbar) +$

$$+ \sum_{n \neq i} w_{i \to n} t = 1$$