Chapter 18 Time Dependent Perturbation Theory

$$i\hbar \frac{\partial}{\partial t}|\psi\rangle = \underset{\sim}{H}|\psi\rangle$$

Split up $\underset{\sim}{H}$ into: $\underset{\sim}{H}^0$ ← • time independent
• soluble, known eigenkets

$+$

"perturbation" $\underset{\sim}{H}'(t)$ ← • possibly time dependent
• "small" compared to $\underset{\sim}{H}^0$

no guarantee an arbitrary $\underset{\sim}{H}$ can be split up like this – but many $\underset{\sim}{H}$ can be

Consider the time dependence of the situation when perturbation is absent.

eigenkets of $\underset{\sim}{H}^0$: $|1^0\rangle, |2^0\rangle, |3^0\rangle, \ldots |i^0\rangle, \ldots$

i for "initial"

$$\underset{\sim}{H}^0|i^0\rangle = E_i^0|i^0\rangle$$

so $$i\hbar\frac{\partial}{\partial t}|i^0\rangle = E_i^0|i^0\rangle$$

assuming that at $t=0$, state of the system $|\psi\rangle = |i^0\rangle$ then

$$|\psi(t)\rangle = e^{\left(-\frac{iE_i^0 t}{\hbar}\right)}|i^0\rangle$$

simple phase factor

no other eigenkets blend in

now conceptually introduce $\underset{\sim}{H}'(t)$. Will the time dependence change, conceptually?

NO → when all the $|i^0\rangle$ are simultaneously eigenkets of $\underset{\sim}{H}'(t)$

when $[\underset{\sim}{H}^0, \underset{\sim}{H}'(t)] = 0$ for all t

phase factor may change: $\underset{\sim}{H}'(t)$ may supplement energy

YES → when $[\underset{\sim}{H}^0, \underset{\sim}{H}'(t)] \neq 0$ this is case we pursue.

Simply expand $|\psi(t)\rangle$ in terms of the eigenkets of $\underset{\sim}{H}^0$

$$|\psi(t)\rangle = \sum_n c_n(t)\,|n^0\rangle$$

were $\underset{\sim}{H}' = 0$, then $c_n(t) = c_n(0)\, e^{\left(-\frac{iE_n^0 t}{\hbar}\right)}$

get from the initial state

wise to factor out the "boring" part of $c_n(t)$, for case $\underset{\sim}{H}' \neq 0$:

$$c_n(t) = \underbrace{d_n(t)}_{\text{"slow \& smooth when } \underset{\sim}{H}' \text{ is small"}}\ \underbrace{e^{\left(-\frac{iE_n^0 t}{\hbar}\right)}}_{\text{"boring"}}$$

$$i\hbar \frac{\partial}{\partial t}\left(\sum_n d_n(t)\, e^{-\frac{iE_n^0 t}{\hbar}}\,|n^0\rangle\right) = \left(\underset{\sim}{H}^0 + \underset{\sim}{H}'(t)\right)\left(\sum_n d_n(t)\, e^{-\frac{iE_n^0 t}{\hbar}}\,|n^0\rangle\right)$$

l.h.s.: chain rule, $\frac{\partial}{\partial t}|n^0\rangle = 0$

$$= \sum_n \left(i\hbar \dot{d}_n(t) + \cancel{E_n^0}\right) e^{\frac{-iE_n^0 t}{\hbar}} |n^0\rangle$$

r.h.s.: $$= \sum_n d_n(t)\left(E_n^0 + \underset{\sim}{H}'(t)\right) e^{\frac{-iE_n^0 t}{\hbar}} |n^0\rangle$$

now bra-in with $\langle f^0|$ $\quad f =$ "final"

on the left hand side, sum collapses, because there are no operators and $\langle f^0|n^0\rangle = \delta_{fn}$ (Kronecker delta)

on the right hand side, $\underset{\sim}{H}'(t)$ becomes a time dependent matrix:

$$\sum_n i\hbar \dot{d}_n(t) e^{\frac{-iE_n^0 t}{\hbar}} \underbrace{\langle f^0|n^0\rangle}_{\delta_{nf}} = i\hbar \dot{d}_f(t) e^{\frac{-iE_f^0 t}{\hbar}}$$

$$= \sum_n d_n(t) e^{\frac{-iE_n^0 t}{\hbar}} \langle f^0|\underset{\sim}{H}'(t)|n^0\rangle$$

define the "transition frequency" $\omega_{fn} \equiv \frac{E_f^0 - E_n^0}{\hbar}$

finally: $$\boxed{\dot{d}_f(t) = \frac{-i}{\hbar} \sum_n \underbrace{\langle f^0|\underset{\sim}{H}'(t)|n^0\rangle e^{i\omega_{fn}t}}_{\text{"matrix"}} \underbrace{d_n(t)}_{\text{column vector}}}$$

$$\begin{bmatrix} \dot{d}_1 \\ \dot{d}_2 \\ \vdots \\ \vdots \end{bmatrix} = \frac{-i}{\hbar} \underbrace{\begin{bmatrix} H'_{11} & H_{12}e^{i\omega_{12}t} & \cdots \\ H'_{21}e^{i\omega_{21}t} & H'_{22} & \\ \vdots & & \ddots \end{bmatrix}}_{\underset{\sim}{H}'} \begin{bmatrix} d_1 \\ d_2 \\ \vdots \\ \vdots \end{bmatrix}$$

again, when $\underset{\sim}{H}'$ diagonal, .. no problem
when $\underset{\sim}{H}'$ not diagonal, two distinct cases:

(1) $[\hat{\underset{\sim}{H}}'(t_1), \hat{\underset{\sim}{H}}'(t_2)] = 0$ for all t_1, t_2

$\Rightarrow$ then only need (conceptually) solve the eigenvalue equation once, diagonalize, integrate to get solution.

(2) $[\hat{\underset{\sim}{H}}'(t_1), \hat{\underset{\sim}{H}}'(t_2)] \neq 0$

$\Rightarrow$ even the nature of the eigenvalue problem is time dependent!

this is actually the more common case!

$\Rightarrow$ do perturbation theory! don't (often) attempt exact solution.

Perturbation

Say at $t=0$, state is purely in i (for initial)

$$d_n(0) = \delta_{ni}$$] 0'th order solution in time.

to <u>zeroth</u> order, either by differentiating the equation just above, or going back to ☆ and ignoring the right hand side as first order,

$$\dot{d}_n(0) = 0$$] 0th order

To solve to first order, plug the 0^{TH} order solution for d_n into RHS of ☆:

$$\dot{d}_f(t) = \frac{-i}{\hbar} \sum_n \langle f^0 | \underset{\sim}{H}'(t) | n^0 \rangle e^{i\omega_{fn} t} \delta_{ni} = \frac{-i}{\hbar} \langle f^0 | \underset{\sim}{H}'(t) | i^0 \rangle e^{-i\omega_{fi} t}$$

This equation is easily integrated. The integration constants are set by

$$d_n(0) = \delta_{ni}$$

so

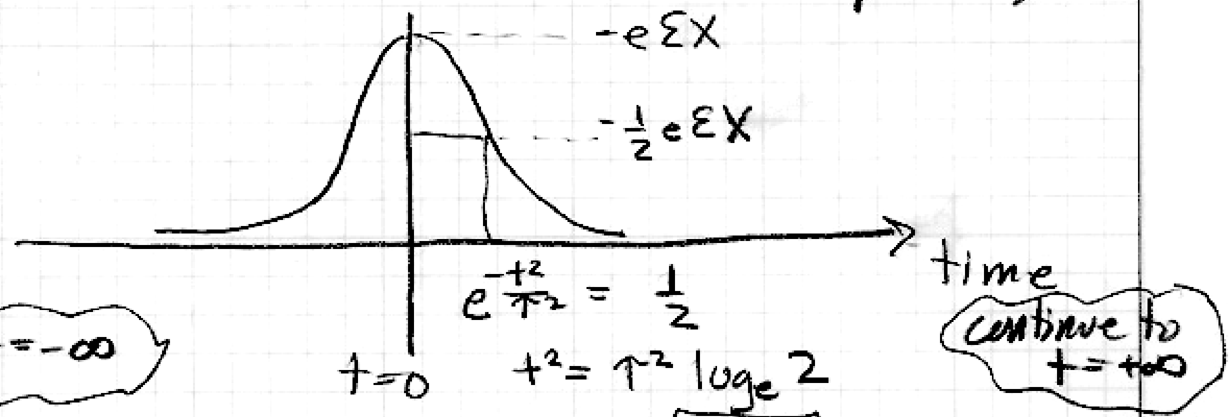
$$\boxed{d_f(t) = \delta_{fi} - \frac{i}{\hbar}\int_0^t \langle f^0 | \underset{\sim}{H}'(t') | i^0 \rangle e^{i\omega_{fi} t'}\, dt'}$$

OK when magnitude of integral term is small compared to 1

<u>example</u>

- simple harmonic oscillator
- $i = 0$ (initial is ground state)

$$\underset{\sim}{H}'(t) = -e\,\mathcal{E}\,\underset{\sim}{X}\, e^{-t^2/\tau^2} \quad \text{(gaussian pulse)}$$



$$e^{-\frac{t^2}{\tau^2}} = \frac{1}{2}$$

$$t^2 = \tau^2 \log_e 2$$

$$t = \tau\sqrt{\log_e 2} = 0.83\cdot\tau$$

Two parts to the computation:

$$\langle f | \underset{\sim}{X} | 0 \rangle = \sqrt{\frac{\hbar}{2m\omega}}\, \langle f | (\underset{\sim}{a} + \underset{\sim}{a}^+) | 0 \rangle$$

$$\underset{\sim}{a}|0\rangle = 0 \qquad \underset{\sim}{a}^+|0\rangle = |1\rangle$$

$$= \sqrt{\frac{\hbar}{2m\omega}}\, \delta_{f1} \qquad E_1^0 - E_0^0 = \hbar\omega$$

$$d_1(\infty) = -\frac{i}{\hbar}(-e\mathcal{E})\int_{-\infty}^{\infty} \sqrt{\frac{\hbar}{2m\omega}}\, e^{-t'^2/\tau^2}\, e^{i\omega t'}\, dt'$$

$$\int_{-\infty}^{\infty} dt' e^{-t'^2/\tau^2} e^{+i\omega t'} = e^{-\frac{1}{4}\omega^2\tau^2}\left[\int_{-\infty}^{\infty} dt' e^{-\frac{1}{\tau^2}(t'-\frac{1}{2}\omega\tau^2)^2}\right]$$

$$-\frac{t'^2}{\tau^2} + i\omega t' = -\frac{1}{\tau^2}\left(t' - \frac{i}{2}\omega\tau^2\right)^2 - \frac{1}{4}\omega^2\tau^2$$

$$\int_{-\infty}^{\infty} dt' e^{-\frac{1}{\tau^2}(t'-\frac{i}{2}\omega\tau^2)^2} = \sqrt{\pi}\cdot\tau$$

$$d_1(\infty) = \frac{ie\mathcal{E}}{\hbar}\left(\frac{\hbar}{2m\omega}\right)^{1/2}(\sqrt{\pi}\,\tau)\, e^{-\frac{1}{4}\omega^2\tau^2}$$

probability: $$\boxed{|c_1(\infty)|^2 = |d_1(\infty)|^2 = \frac{e^2\mathcal{E}^2\pi\tau^2}{2m\omega\hbar}\, e^{-\frac{1}{2}\omega^2\tau^2}}$$

extremal when: $$\frac{d}{d\tau}\left(\tau^2 e^{-\frac{1}{2}\omega^2\tau^2}\right) = 0$$

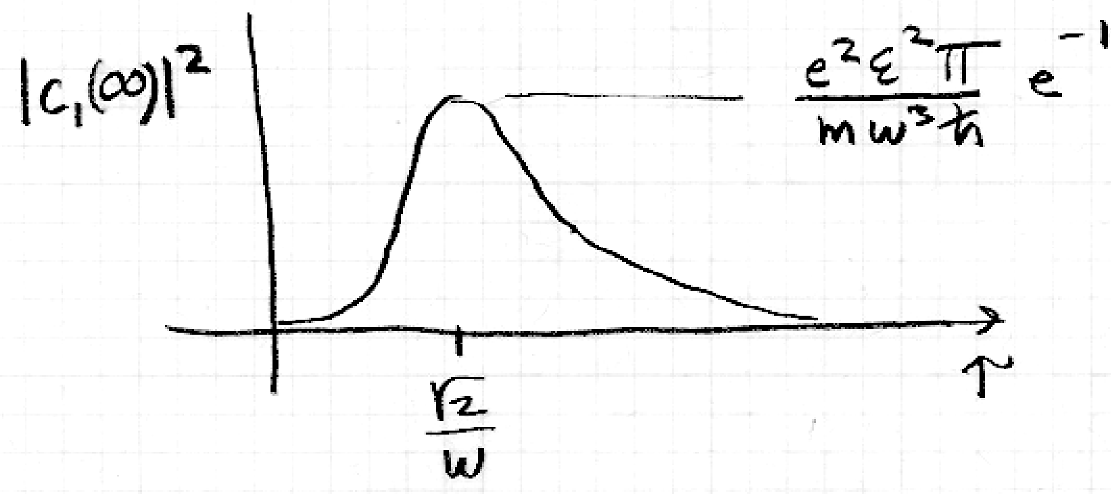
$$\left(2\tau - \tau^2\cdot\omega^2\tau\right)e^{-\frac{1}{2}\omega^2\tau^2} = 0$$

$$\tau\left(2 - \omega^2\tau^2\right)e^{-\frac{1}{2}\omega^2\tau^2} = 0$$

$\tau = 0$
minimum

$\omega\tau = \sqrt{2}$

$$\boxed{\tau = \frac{\sqrt{2}}{\omega} \text{ maximum}}$$



The sudden approximation

Very intuitive: $V_i(x)$ suddenly changes to $V_f(x)$

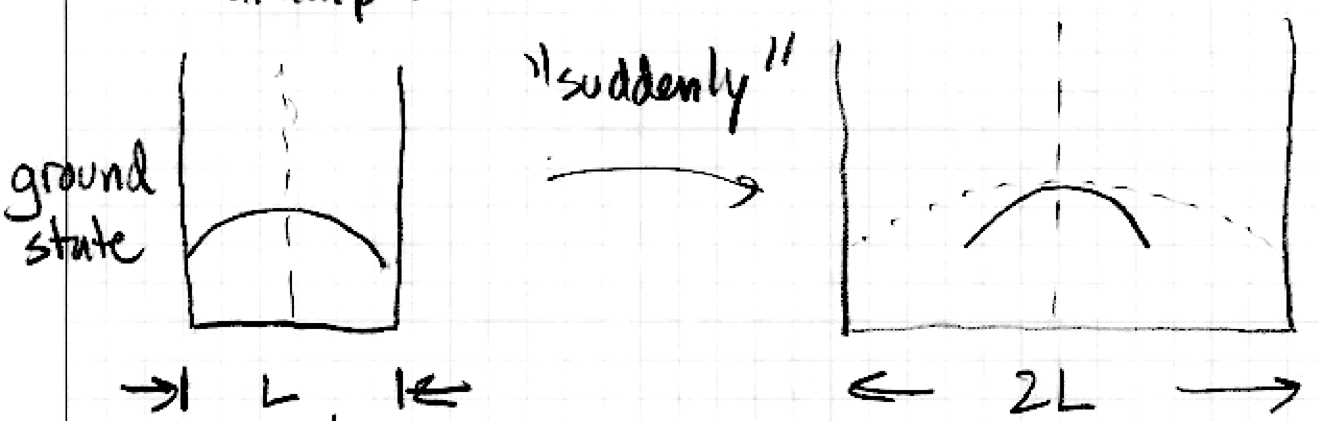
eigenkets of $\underset{\sim}{H}^i$ are $|n^i\rangle$ — eigenkets of $\underset{\sim}{H}^f$ ar $|n^f\rangle$.

If the system, before the change, is in the initial state $|m^i\rangle$, then the probability of finding the system in the final state $|n^f\rangle$ is simply:

$$|\langle n^f|m^i\rangle|^2 = \left|\int d^3x\, \psi_n^{f*}(\vec{x})\, \psi_m^i(\vec{x})\right|^2$$

$\neq \delta_{nm}$ because these are eigenstates of different hamiltonians!

example:



$$\psi_1^i(x) = \left(\frac{2}{L}\right)^{1/2} \cos\left(\frac{\pi x}{L}\right) \qquad \psi_1^f(x) = \left(\frac{1}{L}\right)^{1/2} \cos\left(\frac{\pi x}{2L}\right)$$

$$P(f=1) = \left|\frac{\sqrt{2}}{L} \int_{-L/2}^{L/2} \cos\left(\frac{\pi x}{L}\right) \cos\left(\frac{\pi x}{2L}\right) dx\right|^2$$

let $z = \frac{\pi x}{2L}$ and $\cos 2z = \underbrace{\cos^2 z}_{1-\sin^2 z} - \sin^2 z$

$= 1 - 2\sin^2 z$

$$\int_{-L/2}^{L/2} \cos\left(\frac{\pi x}{L}\right)\cos\left(\frac{\pi x}{2L}\right) dx = \frac{2L}{\pi}\int_{-\pi/4}^{\pi/4} \cos z\,(1-2\sin^2 z)\,dz$$

$\rho \equiv \sin z \quad d\rho = \cos z\, dz$

$z = \pi/4, \; \rho = 1/\sqrt{2}$

$z = -\pi/4, \; \rho = -1/\sqrt{2}$

$$= \frac{2L}{\pi}\int_{-1/\sqrt{2}}^{1/\sqrt{2}} (1-2\rho^2)\,d\rho = \frac{2L}{\pi}\left(\frac{2}{\sqrt{2}} - \frac{4}{3}\frac{1}{2\sqrt{2}}\right)$$

$$= \frac{2L}{\pi}\frac{2}{\sqrt{2}}\frac{2}{3}$$

$$\boxed{P(f=1) = \left|\frac{\cancel{\sqrt{2}}}{\cancel{L}}\cdot\frac{8\cdot \cancel{L}}{\pi\cancel{\sqrt{2}}3}\right|^2 = \left(\frac{8}{3\pi}\right)^2}$$

The art comes in deciding just how long the expansion can take and still be sudden.

$\tau \ll T =$ time for one "bounce"

$$vT \sim \frac{p}{m}T = 2L$$

$$\sim \frac{\hbar k}{m}T = \frac{2\pi\hbar}{m\lambda} = \frac{2\pi\hbar}{2Lm}T = 2L$$

$\tau \ll T \simeq \frac{2mL^2}{\pi\hbar}$ (within a factor of 2 of the text)

A physical example of "sudden" occurs in β-decay:

$$\text{nucleus charge } Z \rightarrow \text{nucleus charge } Z+1 + e^- + \bar{\nu}_e$$

$$^3H \longrightarrow {}^3He^+ + e^- + \bar{\nu}_e$$

for example.

Hydrogenic Eigenstates, $Z=1$ | Hydrogenic Eigenstates, $Z=2$

$\underline{\text{time of } \overset{1s}{\text{system}}} \simeq \dfrac{a_0/Z}{Z\alpha c}$ ↙ distance ↖ electron speed

$$T \simeq \frac{a_0}{Z^2 \alpha c}$$

time it takes the <u>escaping</u> electron to cross out of 1s orbital $\tau \sim \dfrac{a_0}{Zc}$

assume e^- @ speed of light

$$\frac{\tau}{T} = \frac{a_0/Zc}{a_0/Z^2\alpha c} = Z\alpha$$

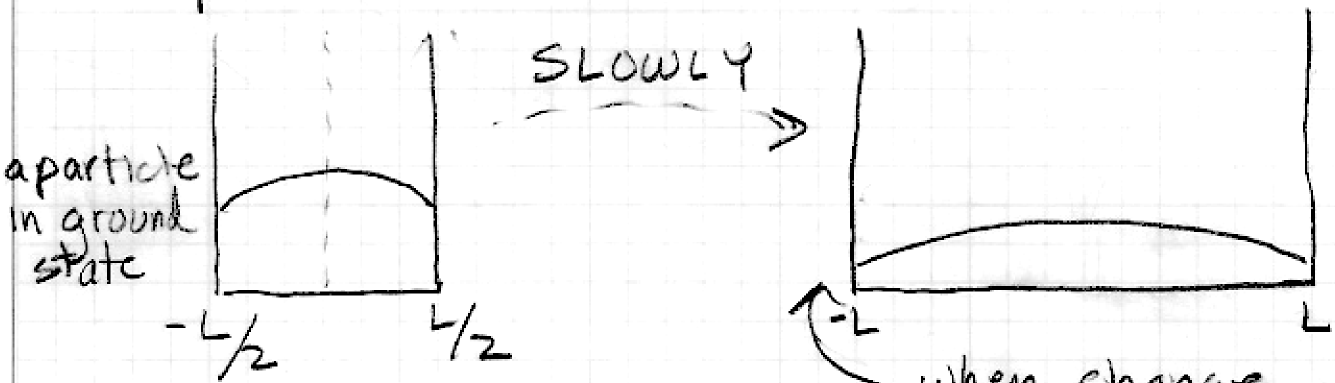
Hydrogen/Helium – "sudden" good

Uranium → "sudden" poor.

Adiabatic Approximation

when Hamiltonian changed slowly, particles tend to stay in the eigenstate that "traces" along

Square Well...



when change from $\pm L/2$ to $\pm L$ goes real slow, the probability of particle staying in the ground state is **1**.

how slow is slow enough?

again, for particle, $mv = p = \hbar k = \frac{2\pi\hbar}{\lambda} = \frac{2\pi\hbar}{2L}$

$$V_{particle} = \frac{\pi\hbar}{mL}$$

$$V_{walls} = \left|\frac{dL}{dt}\right|$$

for adiabatic, want $V_{walls} \ll V_{particle}$

or $\left|\frac{dL}{dt}\right| \ll \frac{\pi\hbar}{mL}$ or $\frac{\hbar}{mL}$

(order of magnitude) π neglected